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VOLUME 37 NUMBER 2 FEBRUARY 1978

CONTENTS

End of Colonialism and the Development of Science Policies for New Nations 65
A. RAHMAN

Reference List of Inorganic & Organic Solids Studied by Wide-Line NMR : Part II 72
N. R. JAGANNATHAN & R. SRINIVASAN

Burning Rate Modifiers for Composite Solid Propellants ... 79
GURDIP SINGH

The Quaternary Structure of Glycoprotein Hormones—Recent Developments 86
M. R. SAIRAM

Reviews 110

Rudolf Peierls and Theoretical Physics: Progress in Nuclear Physics, Vol. 13; The Universe: Geophysics and Astrophysics Monographs, Vol. 11; Practical Techniques for Saving Energy in the Chemical, Petroleum and Metals Industries; Particle Board Manufacture 112

Notes & News ... ...

Holographic fringe stabilization; Heavy ion transfer reactions; New chemical detected in smog formation; Atmospheric ozone monitoring; *Chinese Astronomy;* National Institute of Oceanography, Goa

For Index to Advertisers see Page A 9

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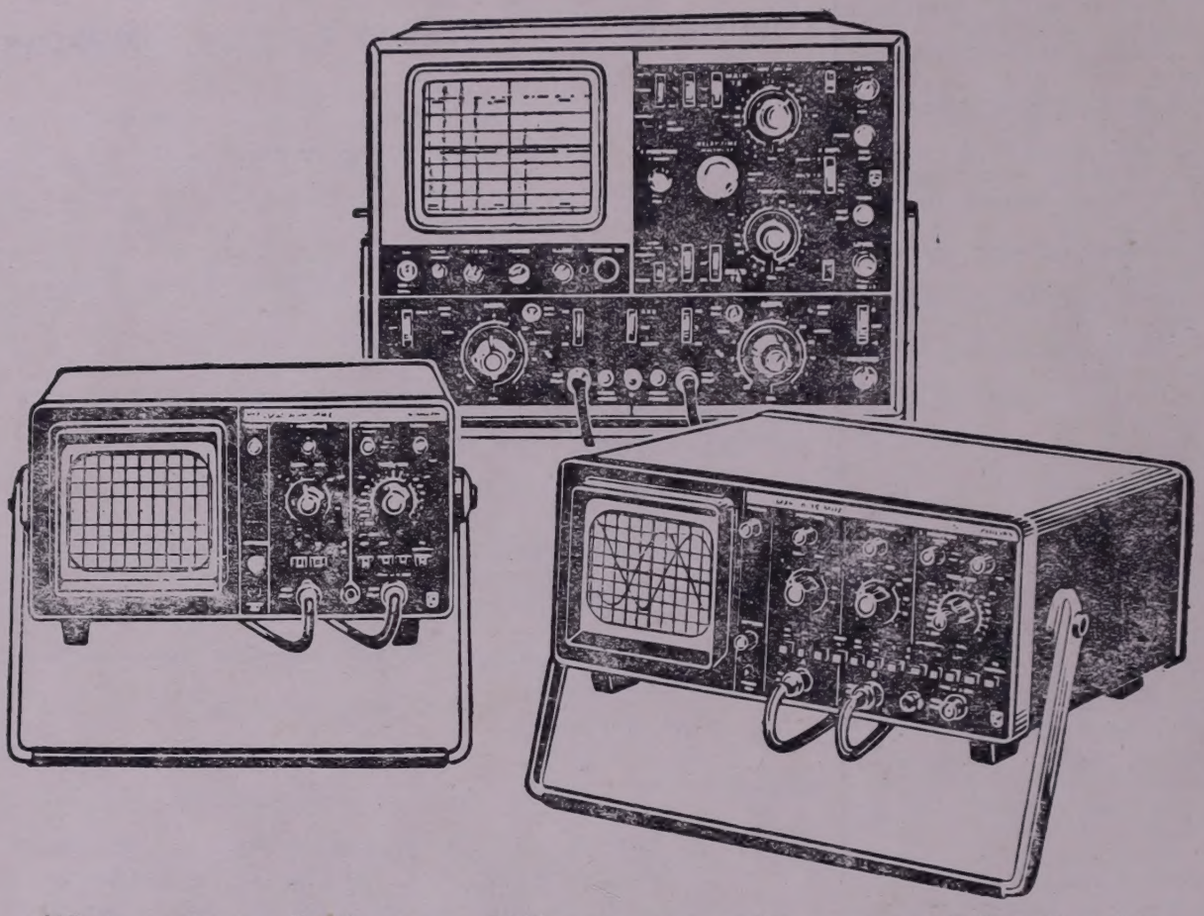

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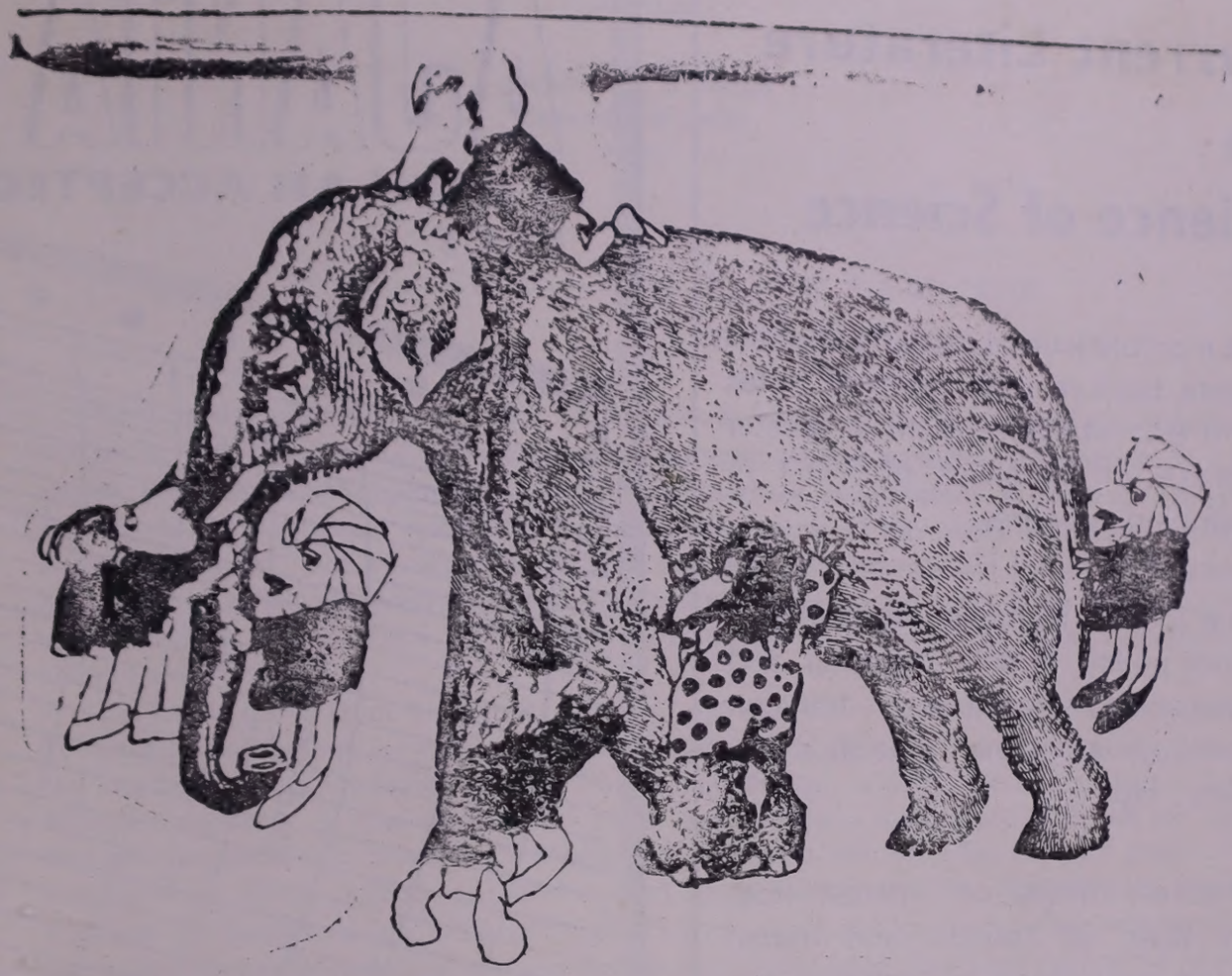

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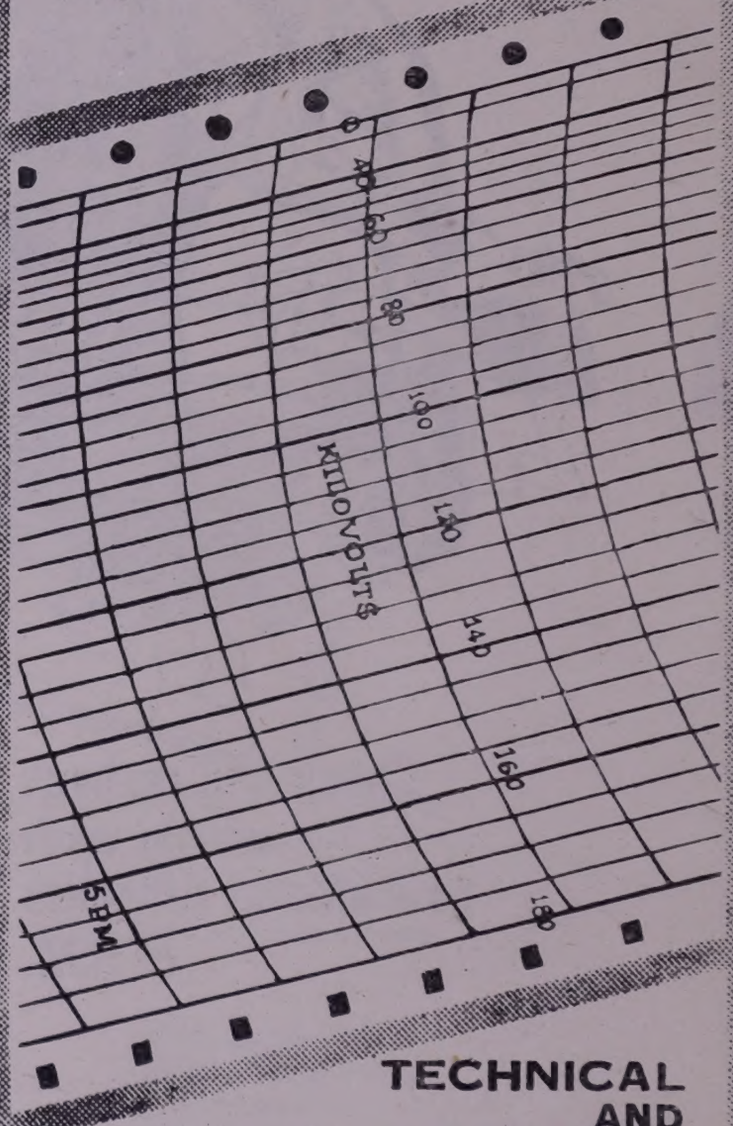

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INDEX TO ADVERTISERS

Chenna Corporation, New Delhi	A6
Current Science Association, Bangalore	A12
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End of Colonialism and the Development of Science Policies for New Nations*†

A. RAHMAN

Centre for the Study of Science, Technology & Development, Council of Scientific & Industrial Research, New Delhi 110 001

Neo-colonialism

THE attainment of political independence by the countries of Asia and Africa was expected to end colonialism, enabling these nations to chart out their own course of development. This, however, does not appear to have happened. Colonialism, as a system through which a country is able to exploit the resource of another country, seems to have continued in a new form. Instead of direct political control or suzerainty over other nations, economic control is being exercised over the new politically independent states of Asia and Africa through various channels. In fact, looking at the exploitation of the resources of the newly independent countries and the degree to which their economy is being shaped by the former colonial powers and certain other western powers, their grip over the developing nations appears to have become firmer.

The nations which have become independent in recent years can be categorized into two groups: (i) those endowed with natural resources which are good foreign exchange earners, and (ii) those which do not possess such resources and depend largely on advanced nations for aid for implementing their development programmes. Majority of the countries in the first category are those with extensive petroleum resources, which they are able to sell, by coming together and bargaining well, at better than throw away prices. The use of the resources generated through the sale of petroleum and its products is, however, another story.

Those countries which do not have the good fortune of having petroleum resources find themselves in a disadvantageous position in bargaining for better prices for export of their materials, including minerals and agricultural products. One or two attempts at bargaining backfired badly.

The disadvantageous situation in which the new nations are placed is evident from the data on trade between the developing and the developed countries (Tables 1-7). These data indicate that the new nations by and large export their natural resources and agricultural produce to the advanced countries and import industrial products from them. In this process, the new nations are the losers.

A recent survey of current economic development conducted by the United Nations[1] brings out the following :

"Because of the weakness of demand in the developed market economies, most primary commodity prices seem likely to decline in the course of 1975, especially in relation to the unit value of manufactured goods whose costs are continuing to rise in the industrial countries. This poses a potential threat to a number of developing countries, especially to the dozen whose debt services ratio (relative to export earnings) is more than twice the average and to some of those that borrowed extensively on the private market in recent years. In view of the large increase in the cost of imports, this will impose a serious liquidity strain on a number of developing countries."

"One sign of impending strain was a sharp increase in the number of countries seeking accommodation from International Monetary Fund. There were 18 in the first quarter of 1975 compared with 10 in the first quarter of 1974 and net borrowing rose from $ 63 million to $ 311 million. And the period saw a number of exchange rate devaluations in Latin America and South and East Asia as well as the imposition of a number of input reducing measures."

The position in which the developing countries find themselves is clear from the following words of Susan George[2]:

"In 1963, says the Government of Tanzania, we needed to produce five tons of sisal to buy a tractor; in 1970, we had to produce ten tons to buy the same tractor. Similarly, a rubber exporting nation could buy six tractors for 25 tons of rubber in 1970, but today only two for the same effort. A cotton growing Sahelian country has to produce two and a half times as much today as in 1960 to import the same low-priced French automobile; cash crops have left the UDC's holding the bag or the begging bowl."

Another dimension has been the change in the economy of some of the developing countries by way of shift from food production to cash crop production for export to advanced countries. As a result of this policy, two things have happened. The best land has been diverted to cash crops which are exported, and as a result the countries have become deficient in food. In order to meet the food requirements, the countries had to import food. The export of cash crops does not even pay for the import of food and the countries are thus placed in a very disadvantageous position. According to Susan George: "Another recent study on Africa shows that in this continent of greatest food deprivation, overall agriculture (meaning cash crops) has done better food production since the early 1950 in every country listed. As late as 1967, the Sahelian country Mali was producing 60,000 tons of food crops. Today, locally produced food amounts to only 15,000 tons, while land devoted to cotton and peanuts has increased dramatically. Even so, in Mali, cash crops export economics do not even cover the price of food imports alone, much less industrial goods[3]."

In this context, two features are worth mentioning.

Firstly, the economy of most of the newly independent nations has been so developed as to make them dependent upon the former colonial powers and the other developed nations for the sale of cash crops and import of food. This dependence is then politically exploited to influence their policies and future development. A large number of countries which

*Contributed to the XV International Congress of the History of Science, Edinburgh, 10-19 August 1977.

†The views expressed in the paper are of the author and not necessarily those of the organization.

TABLE 1 — EXPORT FROM DEVELOPING COUNTRIES TO DEVELOPED COUNTRIES : TOTAL TRADE
(Value in million U.S. dollars)

Exports to→ Exports from ↓	Year	Europe	South Africa	Canada	United States	Japan	Australia Newzealand	USSR
Developing market economies	1970	21960	385	940	10170	6300	710	1690
	1971	24040	305	1260	11990	7280	750	1550
	1972	29040	390	1600	14800	8990	810	1720
	1973	41810	600	1940	20340	15180	1390	2550
	1974	85090	1380	4370	39110	33040	2960	3930
OPEC	1970	8760	245	385	1830	2600	225	150
(Algeria, Ecuador, Gabon, Indonesia,	1971	11690	160	560	2560	3530	180	175
Iran, Iraq, Kuwait, Libyan Arab	1972	14000	240	800	3390	4560	185	285
Republic, Nigeria, Qatar, Saudi Arabia,	1973	20060	405	850	4800	7040	330	430
United Arab Emirates and Venezuela)	1974	55830	1120	2590	15050	21450	1080	760

SOURCE : *United Nations : Statistical Year Book* 1975, U.N., New York, 1976.

TABLE 2 — EXPORT FROM DEVELOPING COUNTRIES TO DEVELOPED COUNTRIES : CRUDE MATERIALS (EXCLUDING FUELS AND OILS AND FATS)
(Value in million U.S. dollars)

Exports to→ Exports from ↓	Year	Europe	South Africa	Canada	United States	Japan	Australia Newzealand	USSR
Developing market economies	1970	3930	31	130	1290	1840	75	550
	1971	3680	32	86	1220	1940	88	530
	1972	4310	51	115	1520	2150	155	475
	1974	—	—	—	—	—	—	—
OPEC	1970	670	—	3	185	195	1	43
	1971	405	—	2	205	190	1	40
	1972	380	6	2	285	255	4	31
	1973	650	5	4	415	520	9	29
	1975	—	—	—	—	—	—	—

TABLE 3 — EXPORT FROM DEVELOPING COUNTRIES TO DEVELOPED COUNTRIES : MINERAL FUELS AND RELATED MATERIALS
(Value in million U.S. dollars)

Exports to→ Exports from ↓	Year	Europe	South Africa	Canada	United States	Japan	Australia Newzealand	USSR
Developing market economies	1970	8320	250	440	2100	2580	275	34
	1971	11280	170	640	3240	3510	275	58
	1972	13580	240	910	4180	4590	240	125
	1973	18250	395	1100	7890	6790	385	270
	1974	—	—	—	—	—	—	—
OPEC	1970	7500	245	365	1420	2110	215	—
	1971	10710	160	550	2110	3270	170	—
	1972	13000	230	780	2830	4190	165	91
	1973	17670	380	930	5780	6180	310	230
	1974	—	—	—	—	—	—	—

TABLE 4 — EXPORT FROM DEVELOPING COUNTRIES TO DEVELOPED COUNTRIES : FOOD, BEVERAGES AND TOBACCO
(Value in million U.S. dollars)

Exports to → Exports from ↓	Year	Europe	South Africa	Canada	United States	Japan	Australia Newzealand	USSR
Developing market economies	1970	5260	21	155	3240	800	93	820
	1971	5000	19	195	3460	900	84	670
	1972	6270	36	200	3810	1050	96	690
	1973	8480	33	245	4380	1660	110	1170
	1974	—	—	—	—	—	—	—
OPEC	1970	420	—	14	195	50	9	87
	1971	365	—	7	210	62	9	120
	1972	395	—	13	225	94	11	115
	1973	520	—	14	300	130	14	135
	1974	—	—	—	—	—	—	—

TABLE 5 — EXPORT OF MACHINERY AND TRANSPORT EQUIPMENT FROM DEVELOPED COUNTRIES TO DEVELOPING COUNTRIES
(Value in million U.S. dollars)

Year	OPEC	Africa	Latin America	Asia		Oceania
				Middle East	Others	
1970	3410	3910	4720	2020	4710	230
1971	4230	5010	5200	2440	5570	230
1972	5510	5700	6150	3520	6120	230
1973	7350	8070	7390	4700	8540	245
1974	11980	10890	10450	8170	12190	300

TABLE 6 — EXPORT OF CHEMICAL PRODUCTS FROM DEVELOPED COUNTRIES TO DEVELOPING COUNTRIES
(Value in million U.S. dollars)

Year	OPEC	Africa	Latin America	Asia		Oceania
				Middle East	Others	
1970	750	860	1310	480	1380	26
1971	880	980	1460	540	1530	29
1972	990	1030	1780	700	1770	37
1973	1430	1420	2290	1020	2640	45
1974	2580	2250	4480	1670	4100	71

TABLE 7 — EXPORT OF "OTHER MANUFACTURED GOODS" FROM DEVELOPED COUNTRIES TO DEVELOPING COUNTIRES
(Value in million U.S. dollars)

Year	OPEC	Africa	Latin America	Asia		Oceania
				Middle East	Others	
1970	2280	2580	2330	1380	4060	180
1971	2630	2750	2440	1680	4510	190
1972	3290	2990	2660	2080	4730	210
1973	4800	3910	3650	3180	6710	240
1974	9260	6360	6850	6370	9140	325

have become thus dependent on the export of their cash crops at increasingly lower prices and import of foodgrains at increasingly higher price become extremely vulnerable economically as well as politically. And as suggested by Lester Brown[4], there is a trend of increase in the vulnerability. According to him, if the trends of past several years continue, the need of 100 importing countries would exceed exportable supply; then the consequence of depending upon one source would have far-reaching effects[4].

Secondly, in the case of both cash and food crops, new varieties have been introduced. These varieties have been developed, by and large, in advanced countries in consonance with their environment, technological level and their capacity to provide the necessary inputs. These varieties require more water, fertilizer and pesticides; in other words, their cultivation is energy intensive. Therefore, while on the one hand the developing countries may not find their cultivation economical at their level of development, on the other, they become dependent on the developed countries for import of machinery, fertilizers and pesticides. As a result, the gain, if any, is offset by the high prices paid for these imports, besides becoming dependent on the developed countries in the bargain.

The experience of India and other countries where green revolution was ushered shows, to their dismay, that when the new varieties were established, the fertilizers were either not available or had to be imported at very high prices.

Another step in the same direction has been the effort to promote the cultivation of new crops in underdeveloped countries instead of improving the production of the traditional cultivated crops. For instance, soyabean cultivation has been promoted in India and some other countries. Massive investments have been made in promotional and extension activities. If the same investments had been made on the improvement of varieties and cultivation of legumes, they would have yielded rich dividends. The advanced countries had a vested interest by way of possessing the technology of processing. Another unfortunate consequence of this policy is that the farmers are lured into diverting the best land for the cultivation of the new crops, since subsidies and other inputs are provided as incentives for doing this.

The extensive control exercised over the mineral resources of the developing countries by the advanced countries also subjects the former to undue pressure in favour of the latter. This is done through transnational companies. According to Obminski[5]: "In Asia too, monopolies are controlling the exploitation and export of tin in Malaysia and Thailand (London Tin Corporation, and other British Companies), crude oil in Cambodia, Malaysia, Indonesia, Thailand (The American Goodyear Tyre and Rubber Co. and British and French Companies) in Brunei and Indonesia (The American Shell Oil, Stanvack and Caltex Companies) and non-ferrous metals in Philippines (The American Consolidated Mine). In Malaysia, foreign capital has in its hand 60 per cent of tin production, some 80 per cent of the exploitation of other useful minerals, and 75 per cent of the production of cautchouc. Over 70 per cent of the import is under the control of foreign capital in which still Britain—the one time metropolitan country—plays the lead. In Philippines, one-third of the share is held by foreigners. Seventy out of 100 largest industrial-commercial companies are under foreign control."

As a result of these investments and profits earned, 2-3 times the amount of capital invested is exported as profits, leaving the developing country poorer than what they were before.

"According to figures for 1961-1970 (basis period 1958-1960), of 87 countries (including the crude oil exporting countries) 63 — with a total population amounting to 81 per cent of the developing countries— lost an yearly average of 2 billion dollars in the sixties which runs up to 9·3 per cent of the annual average of the import of these countries. At the same time, 24 countries drew additional profit of 1·6 billion dollars on the yearly average. Thus, the balance for the decade shows 4 billion dollars, but not to the advantage of the developing countries. To be found among the losing countries are Ghana (124 million), Kenya (28 million), Liberia (87 million), Nigeria (85 million), India (33 million), Indonesia (93 million), Brazil (228 million) and others[6]."

The consequence of these developments have been stated by Obminski as follows:

(1) Control over all phases of production and marketing of products, with a consequential loss of control of the developing countries on their own resources,

(2) Trade mechanisms are operated to the disadvantage of the developing country,

(3) Monopolies severely regulate, through cartel agreements, licensing arrangements and import-export control, any effort by the developing country to become independent, and

(4) Organised sanctions, aimed at destroying the economy of the national state which initiates measures against monopolies.

In addition to the above, as in agriculture so in industry, an elite class is gernerated which develops agriculture as an industry to produce cheap raw materials for advanced countries and local industries, based on imported know-how and to meet the requirements of the transnational corporations and monopolies. This elite class, besides sharing the value system and aspirations of the advanced countries, develops a vested interest and lives as a privileged minority, is urbanized, western educated and has the cultural habits—consumerism—now popular in the advanced countries.

This is in reality similar to the relations that were built during the colonial period, when the resources of the colonies were detached from the internal economic structure and were used for promoting the interests of the colonial power.

The creation of the modern sector industry, as has been pointed out by Harrera[7], follows a pattern. It begins with import substitution, leading to the manufacture of simple consumer goods, then to sophisticated goods and finally incipient heavy

industry. This process is based on the demand created by the privileged minority, and is initiated by the import of know-how and technology. This import, or transfer of technology as it is being called now, is another story of disadvantageous relationship which keeps the developing countries in a state of dependence.

The other result of this development—the process of industrialization—is the creation of the R & D system. This system, as pointed out by Harrera[7], is linked with the modern sector. In view of its linkages, the R & D system is not capable of generating indigenous technology. Some of the consequences of this linkage are:

(1) It is concerned primarily with the adaptation of imported technology.

(2) It is incapable of competing with the advanced countries.

(3) 98% of R & D lies in advanced countries and it is rapidly changing the technologies. The developing countries are at a disadvantage as their R & D systems lean heavily on the advanced countries for import of equipment and instruments and training of personnel. In fact, a large number of trained personnel from developing countries tend to migrate to advanced countries and contribute to R & D of the developed countries, the results of which are exploited to the disadvantage of the developing countries.

(4) The R & D systems created cannot and do not react with the traditional sector, which is the major sector in the developing countries. The result of this lack of interaction is that the traditional sector continues to be based on empirical knowledge, and has no institutional back up to improve the productivity and competitive capability of the indigenous technology. Since the indigenous technology is generally labour intensive, skill development and the consequential betterment of those employed do not take place.

The enclave of modern industry, and the R & D system working for it, meet the demands of the elite minority at the expense of indigenous industry, which is not developed to meet the new demands made on it.

The pressures exerted by the modern sector, with its R & D system, for meeting the needs of the elite, particularly in view of its linkages with the advanced countries, are considerable. These are often achieved in an indirect way through research studies and the direction given to them. A study of the researches carried out in the advanced countries in the area of science policy reveals an interesting pattern in terms of areas investigated in a particular period[8]. The shifts, as is evident from a number of studies, can be stated as general science policy, planning of science, technology transfer, appropriate technology and development models. In the last mentioned area, China studies have come to occupy a major portion. These studies influence decision-making in the developing countries, which unwillingly or otherwise, follow the lines of development suggested for them.

New Perspectives

In considering the recent trends in technology and industry, three factors which are of particular significance to the developing countries arrest the attention.

The first of these, as pointed out earlier by the author[9], is the development of technologies which utilize non-renewable resources for industrial development. As mentioned earlier, the advanced countries exercise considerable control over the resources by virtue of their being in possession of the latest technologies and 98% of R & D. They also control the generation of future technologies. Consequently, there appears to be little chance of developing countries making a breakthrough in attaining self-reliance.

Further, the technologies, and industries based on them, are energy intensive, and are not likely to be productive in some area, e.g. agriculture. According to Susan George[10], "Agriculture as practised in USA today is hardly agricultural at all—it is rather a highly sophisticated, highly energy-intensive system for transforming one series of industrial products into another series of industrial products which happen to be edible." The only snag is that it is sustained at the moment by the resources of the developing countries. This high energy system, where input of energy is more than the output, cannot be sustained for long and is not a model for which the developing countries could go.

Secondly, in the production system, based on the new technologies, there has been a gradual substitution of energy for labour. The use of the existing technologies to develop industries is likely to pose a major problem of employment of people. The developing countries are facing the problems of increasing population and increasing unemployment, including that of the educated people.

Thirdly, there is large scale migration of people from the countryside to urban centres, where more job opportunities exist. This migration is again energy intensive. More people in the cities mean more food to be brought from the countryside to cities, more fuel, greater transport facilities, more hospitals, etc. All these require greater use of energy.

Taking all these trends into consideration, it is evident that the developing countries, if they were to follow in the footsteps of the advanced countries, would not be able to catch up with them, and if they want to be self-reliant, there appears to be no other way for them but to chalk out a different path for themselves.

New Possibilities and Problems

The developing countries, being in a state of low technological development, including lack of adequate scientific and technological manpower, are considerably handicapped in working out a path different from the one being followed by the advanced countries. In fact, they are dependent upon advanced countries to do the thinking for them. A number of studies in advanced countries on intermediate technology, appropriate technology, etc. are indicative of both the ideas and technologies which are investigated and promoted by the advanced countries for developing countries. These are experimented upon in developing countries and the experiences gained are incorpora-

ted in the new developments, and the technologies thus developed are then sold at high cost and under unfavourable terms and conditions to the developing countries. It would be interesting to know how many of such projects, such as water desalination, growing of vegetable, fruits, etc. in West Asia, are being pursued in the developing countries, either at the expense of the latter or being subsidised through UN agencies and what benefit advanced countries and multinational corporations have derived from such projects, as compared to the developing countries. It would also be of interest to know as to how these projects were selected, who is likely to be the beneficiary in the developing countries and how they have affected the economies of the countries concerned.

A major hurdle in the way of developing countries arises out of the conceptual framework of the scientists in the developing countries. They are trained in advanced countries, and the nature of training is such that each of them sees the problem from purely technical angle, from the point of view of his narrow field of specialisation, while the problems faced are multidisciplinary in nature. Having imbibed the lore and culture of science of the advanced countries, they see only those areas of research which are under investigation in advanced countries and wish to replicate them in their own country. In doing so, a major investment is made in building up technical facilities for work comparable to that in the advanced countries. In this they are helped by their former colleagues in the advanced countries. This is to the advantage of the instrument manufacturers of the advanced countries. The sale of instruments, which may run into billions of dollars, their actual use and the benefit derived from them, would be an interesting study in itself.

Some New Trends

As a result of experience of the newly independent countries over the last 30 years, certain new trends have emerged.

(1) There is a shift away from the practice of building institutions in the image of institutions of teaching and research of the advanced countries. It is now being increasingly recognized that the institutions to be established are to be in consonance with the tasks they have to perform, and that their excellence is not an abstract quantity; it has to be evaluated in terms of the role they play in the context of the social situation and the attainment of goals set before them.

(2) Science is now being increasingly recognized as an instrument of social change. Consequently, efforts are being made to understand its socio-economic and political linkages and utilize this understanding in developing science and technology to attain a set of socio-economic and political objectives.

(3) It is being increasingly recognized that purely technical factors should not be taken into account in the choice of problems and in implementing the results of research, but other economic, social, political cultural, moral, ethical and environmental factors are also required to be taken into account in deciding the areas of research as well as in applying results of research, i.e. in developing technologies and creating industries based on the latter.

As a result of this recognition, techniques are being developed to quantify and incorporate these factors into detailed thinking on problems. One area where some progress has been made is 'technology assessment'. Another area which is receiving considerable attention is 'technological forecasting', which is no more limited to the projection of the present trends, but includes such areas as predicting the possible socio-economic or cultural effects of an invention with a view to evaluating and deciding what should be done with the harmful effects.

(4) There is a widespread appreciation of the fact that despite considerable possibilities, scientific researches and their application have not resulted in amelioration of the lot of the people. In fact, the growth of science and technology has strengthened the position of advanced countries *vis-a-vis* the developing countries. Further, within the developing countries, an elite class has emerged, which has more in common with their counterparts in the advanced countries than with their countrymen. While the poverty in the country and the problem facing it have continued to grow, the elite class has continued to prosper and increase its power. This has led some scientists to ask the question: Science at what cost and for whose benefit?

These developments are a healthy sign and are indicative of the maturity of the scientists and technologists of the developing countries. However, the impact of these trends would depend upon the following three factors:

(1) An important factor is the extent to which the scientists are able to develop methodologies and technologies to convert aspirations into social programmes, later into concrete programmes of research and the degree to which they are able to utilize results of research in developmental programmes.

The situation, as it exists today in the developing countries, is that establishment science, with its linkages with the science of the advanced countries represents almost 98% of the science of the developing countries and gets nearly all the resources which are available within each country. Those who are thinking on new lines are dispersed and are making lone efforts, which are sub-critical. Therefore, unless these individual efforts are merged and viable groups established, the results would not be effective.

(2) Though there is substantial scientific manpower in the developing countries, there is, unfortunately, no scientific community. These scientists are steeped in the culture of science of the advanced countries as well as addicted to the traditional pattern of their respective countries. They are divided in various groups, each group centred around various people in position of power, and a few of them highly political. The result is that no common programme around which scientists could be brought together can be evolved, nor a common code of conduct or ethics could be developed to bind the scientists into a community. As a result, a number of important problems of science and technology go unattended, much to the detriment of science and technology,

as well as their application to the problems of development. While important porblems go unattended, much heat is generated through controversies which are initiated in advanced countries and are relevant to them rather than to the developing countries and when effort is made to apply them to the latter, the issue get distorted.

(3) Despite the fact that nearly all the developing countries have institutional frameworks in terms of councils, departments of science and technologies to frame policies and advise the governments, institutions for research, etc. these are not fully integrated with other policies. There is an impression that the role of science and technology in the process of development is not fully appreciated. While the infrastructure of science and technology is maintained, technology is imported from advanced countries and further development is generally guided by this.

New Tasks

In the context of the situation discussed above, two major tasks emerge. The first of these is concerned with science policy studies and the second with the possible role which science policy scientists could play.

The development of science policy studies emerges as a major task in the developing countries, particularly in view of the fact that these studies could play a crucial role in integrating different branches of science in looking at problems and in bringing together natural and social science in developing a proper perspective of science, and assessment of the impact of science on man, society and environment. In other words, it has become central to the planning process.

For persons in the field of science policy to assume such a role and to be in a position to discharge it effectively, efforts are needed in a number of areas pertaining to (i) techniques of collection of information its storage and retrieval and easy availability, techniques of anlysis of the information and its effective utilization in decision-making; (ii) evolution of comparable methodologies and techniques in natural and social science with a view to utilizing the results of researches from the respective areas in the decision-making process; (iii) development of techniques to quantify factors which are considered qualitative or otherwise develop methodologies to incorporate effectively non-quantitative factors into the analysis of the situation, so that the importance and relevance of these factors are not ignored in the decision-making process; and (iv) subject science policy studies carried out so far as well as scientific, technological and developmental programmes to critical analysis, with a view to understanding their social and economic content, cultural factors involved and relevance in relation to goals set and time taken to achieve them.

The role of science policy scientists could be of critical significance in bringing natural and social scientists together and developing a common language. Further, they can be an effective link between the scientists and planners by making the latter appreciate the role which indigenous science and technology could play in the process of development and by persuading them to take indigenous science and technology as an essential element in the process of development.

The most important role which science policy scientists could play is through the creation of public awareness of the role of science and technology in society. Each decision to make a major investment in a branch of science or technology or the latter's application may mean denying investment to another field of activity. This may affect not only the present day development, but also the future pössibilities. Science policy scientists could play a major role in making people aware of the consequences of such major decisions and their impact on man, society and environment and create public opinion against those with affect these adversely.

Besides playing the role of science and technology critics, they could also be helpful in pointing out major gaps in research and development which require attention. In scientific and technological research, those branches which are already established tend to get all the resources at the expense of those which may be developing or may be of considerable significance to future developments; this has been true of biology in recent years. Science policy scientists can keep on focussing attention of the decision-makers to such problems.

Most of the developing countries are still dominated by the old concept of popularization of science, whereby "marvels" and "miracles" of science and technology are explained to people through such media as exist in the country. This approach may have had some impact in creating curiosity about science or technology, but it had one disastrous effect, that of creating a gulf between science and the traditional culture. In most of the developing countries, the traditional culture, with its sociological practices and outlook based on antiquated ideas and knowledge, continues side by side with the technologies which have been imported or introduced in the country and often these technologies are used to reinforce the traditional culture, as is the case with radio and television.

A significant role of science policy scientists could be in making science and technology a part of the culture of the developing countries, and thus to do away with the existing two cultures. This is possible through the understanding of traditional culture in its historical context with its scientific and technological base, appreciation of the contemporary problems faced by the people and by interacting with them for explaining them and for finding alternatives. In other words, this means delinking science from the service of the elite and utilizing it for solving problems of the poor. In doing so, they would take away quite a bit of the mystique that has been built around science and technology.

Science and technology are not subjects of much public debate in the developing countries. Consequently, investment in science is a matter of adjustment between the practitioners of science and the bureaucracy and politicians. As a result, one often finds glaring anomalies in the funding of science, the latter going to prestigeous rather than relevant

areas. Normally those areas which are currently most advanced in the developed countries are considered prestigeous areas. Any effort to make science a part of public debate is not encouraged under the slogan "let us not politicalise science". Science policy scientists can play a vital role in making science a part of public debate. This is essential to end the esoteric character of science in the developing countries.

In the developing countries there are very few scientists who have a social perspective or are engaged in science policy studies. It is necessary for them to collaborate effectively between themselves. This is all the more necessary, as they have common problems. This will effectively cut across their isolation as well as help to overcome the limitations arising from inadequacy of resources.

In conclusion, it may be relevant to quote General Lee, who led the Southern armies in the American civil war. When approached in his retirement and asked about the future, he is supposed to have said: "The tasks before humanity are so great and the means available so meagre that we often see only the ebb of the advancing wave and get discouraged. It is history that teaches up hope."

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Reference List of Inorganic & Organic Solids Studied by Wide-Line NMR : Part II*

N. R. JAGANNATHAN & R. SRINIVASAN

Department of Crystallography & Biophysics, University of Madras, Guindy Campus, Madras 600 025

A list of inorganic and organic compounds studied by wide-line NMR (excluding metals) for use as ready reference material has been published by Ganapathy and Srinivasan[1]. The list covered 91 inorganic and 78 organic compounds up to about 1972. The present list is supplementary to the earlier one and covers the literature survey up to the middle of 1976, although a few entries belong to the end of 1976. All the remarks and symbols used in the earlier publication apply equally for the current data and this paper may, therefore, be treated as Part II and a continuation of the earlier one referred to as Part I. Accordingly, Tables 1A and 2A, which include 59 inorganic and 118 organic entries respectively, are essentially continuations of Tables 1 and 2 of Part I and deal with inorganic and organic compounds respectively.

However, one new feature, viz. the characterization of the type of study has been added in the current list. The information as to whether the particular study in the solid state is by continuous wave technique (denoted by CW) or by pulse method (denoted by PM) has also been incorporated in the tables.

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*Contribution No. 474 from the Department of Crystallography & Biophysics, University of Madras, Guindy Campus, Madras 600 025.

TABLE 1A — LIST OF INORGANIC SOLIDS STUDIED BY WIDE-LINE NMR

Name of the compound	Chemical formula	Method of study	Resonant nucleus and type of information	Reference
Ammonium bromide*LT	NH_4Br	CW	$^{1}H^{b}$	2,3
Ammonium dihydrogen arsenate*†LT	$NH_4H_2AsO_4$	PM	$^{1}H^{b}$	4
Ammonium hexafluorogermanate*LT	$(NH_4)_2GeF_4$	PM	$^{1}H,^{19}F^{b}$	5
Ammonium hexafluorophosphate*LT	NH_4PF_6	CW, PM	$^{1}H,^{19}F^{a,b}$	6,7
Ammonium iodate*LT	NH_4IO_3	CW	$^{1}B^{b}$	2
Ammonium ions (Tunneling of)*LT	$(NH_4)_2PbCl_6$	CW	$^{1}H^{b}$	8
Ammonium perchlorate*LT	NH_4ClO_4	CW	$^{1}H^{b}$	9
Boron trifluoride monoethylamine*LT	$BF_3.Me.NH_2$	CW	$^{1}H,^{19}F^{b}$	10
Boronoxide†LT	B_2O_3	PM	$^{11}B^{b}$	11
Borontrifluoride, mono and dihydrates†LT	(a) $BF_3.H_2O$ (b) $BF_3.2H_2O$	CW	$^{1}H,^{19}F^{b}$	12
Carnallites hydrates†		CW	$^{1}H^{b,d}$	13
Cesium lead trifluoride*LT	$CsPbF_3$	CW	$^{19}F^{b}$	14
Chlorine pentafluoride	ClF_5	CW	$^{19}F^{b}$	15
Cobalt chloride hexahydrate†	$CoCl_2.6D_2O$	CW	$^{1}H^{b,c}$	16
Copper tuttonsalts*LT	$Cu_xI_{n1-x}^{o}$ $Cs_2(SO_4)_2.6H_2O$	PM	$^{1}H^{a,b}$	17
Cuprous halides*LT		PM	$Cu,^{65}Cu$ $^{81}Br^{b}$	18
Deuterated lanthanum hydride		CW	$^{1}H^{b}$	19
EnclathratesLT	SF_6 and SF_4	CW	$^{19}F^{b}$	20
FerrocenesLT		CW	$^{1}H^{a,b}$	21
Germane*LT	GeH_4	PM	$^{1}H^{b}$	22
Germanium fluoride*	GeF_4	CW, PM	$^{19}F^{b}$	23
Hexahydrated chlorostannates of nickel†	$NiSnCl_6.6H_2O$	CW	$^{1}H^{b,d}$	24
Hexahydrated chlorstannates of copper†	$CuSnCl_6.6H_2O$	CW	$^{1}H^{b},d$	24
Hexahydrated fluorosilicates †LT	(a) $MSiF_6.6H_2O$ (M=Mg, Zn, Cu,Ni,Co) (b) $CuSiF_6.6H_2O$	CW	$^{1}H,^{19}F^{b}$	25,26
Hafnium oxochloride*LT	$HfO\ Cl_2.nH_2O$	CW	$^{1}H^{b}$	27
Hydrated sodium & potassium-metavanadatesLT	$NaVO_3.2H_2O$ $KVO_3.H_2O$	CW	$^{51}V,$ $^{23}Na^{a,b,c}$	28
Krypton* (solid)	Kr	PM	$^{83}Kr^{a,c}$	29
Lead dicalcium propionates*	$Ca_2Pb(EtCO_2)_6$	PM	$^{1}H^{b}$	30
Lithium iodate†LT	$LiIO_3$	CW	$^{7}Li^{a,b}$	31
Lithium cupric chloride dihydrate†	(a) $LiCuCl_3.2H_2O$ (b) $LiCuCl_3.2D_2O$	CW	$^{1}H,^{2}H^{d}$	32
Lithium sulphate monohydrate†	$LiSO_4.H_2O$	CW	$^{7}Li^{d}$	33
Magnesium chloride hexahydrate	$MgCl_2.6H_2O$	CW	$^{1}H^{d}$	34
Methylammonium chloride*(solid phases)		PM	$^{1}H^{b}$	35
Metal ammonium compounds*LT		CW	$^{1}H^{a,b}$	36
Monomethylammonium chloride*LT		CW, PM	$^{1}H^{b}$	37
Natrolite*†LT	$Na_2Al_2SiO_3.2H_2O$	CW	$^{1}H^{27},Al^{b,d}$	38
Octahydrotriborateanions	(a) $Me_4NB_4H_8$ (b) KB_3H_8	CW	$^{11}B^{b,c}$	39
Penta-decamethoriumLT		CW	$^{1}H^{b}$	40
Phosphorus sesquisulphide*LT	P_4S_3	CW	^{31}Pb	41
Phosphorus-tungsten-vanadium heteropolyacid		CW	$^{1}H^{b}$	42
Potassium hexafluorophosphate*LT		PM	$^{19}F^{b}$	43
Potassium tetraflurocuprate†	K_2CuF_2	CW	$^{19}F^{a}$	44
Potassium tetrafluoromanganate*	K_2MnF_4	CW	$^{19}F^{b}$	45
Potassium trifluorocuprateLT	$KCuF_3$	CW	$^{19}F^{a}$	46

Contd

TABLE 1A — LIST OF INORGANIC SOLIDS STUDIED BY WIDE-LINE NMR—*Contd*

Name of the compound	Chemical formula	Method of study	Resonant nucleus and type of information	Reference
Silane*LT	SiH_4	PM	$^{1}H^{b}$	47
Sodium hexafluorophosphate*LT		PM	$^{19}F^{b}$	43
Sodium hydrosulphideLT		PM	$^{23}N^{a,b,c}$	48
Strontium dicalcium propionates*	$Ca_2Sr(Et\ CO_2)_6$	PM	$^{1}H^{b}$	30
Rubidium hexaflurophosphaet*LT		PM	$^{19}F^{b}$	43
Tetraatomic phosphorus*LT		PM	$^{31}P^{b}$	49
Tetrafluorides*		CW	$^{19}F^{b}$	50
Tetrafluorosilane*	SiF_4	CW,PM	$^{19}F^{b}$	51
Tetraamine cobalt complexes*LT		CW	$^{1}H^{b}$	52
Ternary alkali metal silicate and alkali metal borate glasses		CW	$^{23}N^{a}$, $^{7}Li^{b,c}$	53
Trimethylaminogallene*LT	H_3GaNMe_3	CW,PM	$^{1}H^{b}$	54
Uranium hydrideLT	β-UH_3	PM	$^{1}H^{b}$	55
Vanadium†		CW	$^{50}V^{b}$	56
Zeolites		CW,PM	$^{1}H^{b}$	57
Zirconiumoxochloride*LT	$ZrOCl_2.\ nH_2O$	CW	$^{1}H^{b}$	58

* indicates the study of polycrystalline compounds.
† indicates the study of single crystals.
LT denotes the studies at low temperature
The type of information is indicated by a,b,c and d, where 'a' refers to structural information, 'b' to the study of molecular motions, 'c' to the study of quadrupole effects, and 'd' to the study of water molecules in hydrated crystals.

TABLE 2A — LIST OF ORGANIC SOLIDS STUDIED BY WIDE-LINE NMR

Name of the compound	Chemical formula	Method of study	Resonant nucleus and type of information	Reference
Acenapthalene*LT		CW	$^{1}H^{b}$	59
Acenapthalene-S-trituitrobenzene complexes*LT		CW	$^{1}H^{b}$	59
AcetoneLT	$CH_3.CO.CH_3$	CW,PM	$^{1}H^{b}$	60
Acetone clathrate deuterateLT		CW,PM	$^{1}H^{b}$	60
Acetylene*	C_2H_2	CW,PM	$^{1}H^{b}$	61
Acylic aromatic amides*		CW	$^{1}H^{b}$	62
Alanine*LT	$C_3H_7NO_2$	CW,PM	$^{1}H^{b}$	63
Amino acids*		CW	$^{1}H^{b}$	64
Aminobenzoic acid-*p**	p-$H_2NC_6H_4CO_2H$(S)	CW	$^{1}H^{b}$	65
Aminobutyric acid-γ*LT		CW	$^{1}H^{b}$	66
Aminophenol-*p**LT	p-$H_2NC_6H_4OH$	CW	$^{1}H^{b}$	67
Aminophenol-*n**LT	n-$H_2NC_6H_4OH$	CW	$^{1}H^{b}$	68
Aminopyridine-4*LT		CW	$^{1}H^{b}$	69
Ammonium tartrate*	$(NH_4)_2C_4H_4O_6$	PM	$^{1}H^{a,b}$	70
Anthranilic acid*LT	$C_6H_4NH_2COOH$	CW	$^{1}H^{b}$	71
Aromatic amines*LT	(a) p-$H_2NC_6H_4C_6H_4NH_2$	CW	$^{1}H^{b}$	72
Aspartic acid*LT	(b) p-$H_2NC_6H_4CO_2H$. $C_4NH_7O_4$	PM	$^{1}H^{b}$	73
Azabicyclononane-3		CW,PM	$^{1}H^{b}$	74
Benzene*	C_6H_6	PM	$^{1}H^{b}$	75

Contd

TABLE 2A — LIST OF ORGANIC SOLIDS STUDIED BY WIDE-LINE NMR — *Contd*

Name of the compound	Chemical formula	Method of study	Resonant nucleus and type of information	Reference
Benzaldehyde (dimethylamino)-*p*LT	*p*-$Me_2NC_6H_4CNO$	CW	$^1H^b$	76
Benzil*LT		CW	$^1H^b$	71
bis (cyclooctatetranene) iron†LT		CW	$^1H^b$	77
Butadiene-1,3LT		CW	$^1H^b$	78
Copper complexes of pyrazine*LT		CW	$^1H^b$	79
Crystalline amino acids		PM	$^1H^b$	80
Cycloheptaneone		CW	$^1H^b$	81
Cyclohexanone		CW	$^1H^b$	81
Cyclohexane(trifluoromethyl) and its derivatives		PM	$^1H,^{19}F^b$	82
Cyclonomanone		CW	$^1H^b$	81
Cyclooctanone		CW	$^1H^b$	81
Cystine*LT	$C_6H_{12}N_2O_4S_2$	PM	$^1H^b$	73
Deuterated trimethyl acetic acid*LT	$(CH_3)_3CCOOD$	CW,PM	$^1H^b$	83
Dimethylamine*LT	$(C_2H_5)_2NH$	CW,PM	$^1H^{a,b}$	84
Diethylamineclathrate deutrate*LT	EtNH	CW,PM	$^1H^{a,b}$	84
Dimethoxy benzaldehyde-2,4*LT		CW	$^1H^b$	85
Dimethyl sulphoxide*LT	$(CD_3)_2SO$	PM	$^1H^b$	86
Diethylazoxybenzoate‡		PM	$^1H^b$	87
Dimethylamine in the condensed and clathrate deuterate phases		CW	$^1H^b$	88
Dimethylacetylene†LT	MeC:CMe	CW,PM	$^1H^b$	89
Dimethylbutane-2,3†LT	$Me_2CHCHMe_2$	CW	$^1H^b$	90
Dimethoxybenzaldehyde-3,4*LT	$C_6H_3(OCH_3)_2CHO$	CW	$^1H^b$	91
Esters*	R-$COOCH_3$	CW	$^1H^b$	64
Ethane*LT	C_2H_6	CW,PM	$^1H^b$	92,93
Glycine*LT	$CH_2.NH_2.COOH$	PM	$^1H^b$	73
Glycine-α	$C_2NH_5O_2$	PM	$^1H^b$	80
Halothane-trithymotide clathrate*LT	$CH_3CHClBr$-tri-O-thymotide clathrate	CW	$^{19}F^b$	94
Hexamethylethane*	C_8H_8	PM	$^1H^b$	95
Hexafluorobenzene	C_6F_6	CW	$^1H^b$	96
Hippuric acid*		CW	$^1H^b$	97
Histidine*LT	$C_9H_9N_3O_2$	PM	$^1H^b$	73
Hydrazine*LT	N_2H_4	CW	$^1H^b$	98
Hydroquinone clathrate†		CW	$^1H^{b,d}$	99,100
Imidazole†LT	$C_3N_2H_4$	CW	$^1H^b$	101
Isoleucine*LT	$C_6H_{13}NO_2$	PM	$^1H^b$	63
Leucine	$C_6H_{13}NO_2$	PM	$^1H^b$	63
Lithiumformate monohydrate†	$O_2CH.H_2LiO$	CW	$^7Li^d$	102
Metalamine cynide-aromatic clathrate		CW	$^1H^a$	103
Methane*LT	CH_4	CW,PM	$^1H^b$	104
Methionine*LT	$C_5H_{11}NO_2S$	PM	$^1H^b$	63
Napthalene complexes	$C_{10}H_8$	CW	$^1H^b$	105
Neopentane†		PM	$^1H^b$	106
Nitrophenol-*p*LT	*p*-$NO_2C_6H_4OH$	CW	$^1H^b$	107
Nitrotoluene-*p*	*p*-$C_6H_4(CH_3)NO_2$	CW	$^1H^b$	108
Nonadecane-n*	$C_{19}H_{40}$	CW	$^1H^b$	109
Norbornane	C_7H_{12}	PM	$^1H^b$	74, 110
Norbornadiene	C_7H_8	PM	$^1H^b$	74,110
Norbornylene		PM	$^1H^b$	74,110
Norleucine*LT		PM	$^1H^b$	63
Organic plastic crystals†		PM	$^1H^b$	110
Oxalic acid dihydrate	$C_2H_2O_4.2H_2O$	CW	$^1H^b$	111
Pentaerythritol	$C_5H_{12}O_4$	CW	$^1H^b$	112

Contd

TABLE 2A — LIST OF ORGANIC SOLIDS STUDIED BY WIDE-LINE NMR—*Contd*

Name of the compound	Chemical formula	Method of study	Resonant nucleus and type of information	Reference
Phloroglucinol*LT	$1,3,5\text{-}C_6H_3(OH)_3$	CW	$^1H^b$	113
Phthaladehydic acid*LT		CW	$^1H^b$	114
Phenol[LT]	C_6H_5OH	PM	$^1H^b$	115
Polyethylane	$(CH_2)_n$	CW	$^1H^b$	116
Polycarbonate		CW	$^1H^b$	117
Polyisobutylene[LT]		CW	$^1H^b$	118
Poly-L-analine*LT		PM	$^1H^b$	119
Poly-L-leucine*LT		PM	$^1H^b$	119
Poly-glycine*LT		PM	$^1H^b$	119
Poly-L-valine*LT		PM	$^1H^b$	119
Propellane		PM	$^1H^b$	120
Protocatechualdehyde*LT	$C_7H_6O_3$	CW	$^1H^b$	121
Pyrene (complexes)*	$C_{16}H_{10}$	CW	$^1H^b$	96
Pyromethilicdianhydride	$C_{10}H_2O_6$	CW	$^1H^b$	122
Quinol clathrates		CW	$^1H^b$	123
Serine*LT	$C_3H_7NO_3$	CW,PM	$^1H^b$	124
Solid isomers				
(a) Twistane	$C_{10}H_{16}$	CW	$^1H^b$	125
(b) Adamentane				
Tetraethylammonium bromide*LT	$Et_4N^+Br^-$	CW	$^1H^b$	126
Tetracynobenzene	$C_{10}N_2H_4$	CW	$^1H^b$	127
Tetracyanoethylene	C_6N_4	CW	$^1H^b$	127
Tetrabutylammonium iodide*LT		CW	$^1H^b$	128
Tetramethylammonium bromide*	$(CH_3)_4NBr$	CW,PM	$^1H^b$	129
Tetramethylammonium compounds*LT		CW	$^1H^b$	130
Tetramethylphosphonium bromide*LT	$(CH_3)_4PBr$	CW,PM	$^1H^b$	131
Tetramethylphosphonium chloride*LT	$(CH_3)_4PCl$	CW,PM	$^1H^b$	131
Tetramethyl phosphonium iodide*LT	$(CH_3)_4PI$	CW,PM	$^1H^b$	131
Tetramethyl-ammonium-cadmium chloride*	Me_4NCdCl_3	CW,PM	$^1H^b$	132
Tert-butylamine clathrate deutrate*LT		CW,PM	$^1H^b$	133
Tert-butylamine*LT		CW,PM	$^1H^b$	133
Threonine*LT	$C_4H_9NO_3$	CW,PM	$^1H^b$	63
Threonine and its isomers*		CW	$^1H^b$	134
Tribromoaniline-2,4,6*LT	$C_6H_4Br_3N$	CW	$^1H^b$	135
Triethylene diamine		PM	$^1H^b$	74
Triglycine fluoroberyllate*		PM	$^1H^b$	136
Trimethylacetic acid (or) Pivalic acid*		CW,PM	$^1H^b$	83
Trimethylamine*LT		CW,PM	$^1H^b$	142
Trimethyl phosphine*LT		CW,PM	$^1H^b$	142
Trimethylamine-trimethylborne*LT		CW,PM	$^1H^b$	137
Triphenyltin bromide*LT		CW,PM	$^1H^b$	138
Triphenyltin-fluoride*LT		CW,PM	$^1H^b$	138
Triphenyltin-chloride*LT		CW,PM	$^1H^b$	138
Triphenyltin hydroxide*LT		CW,PM	$^1H^b$	138
Tritriacontane-4*n*	$n\text{-}C_{33}H_{68}$	CW	$1H^b$	139
Tryptophan*LT	$C_4H_7N_2COOH$	PM	$^1H^b$	73
Tyrosine*LT	$C_9H_{11}NO_3$	PM	$^1H^b$	73
Urea†LT	NH_2CONH_2	CW	$^1H^b$	140
Valine*LT	$C_5H_{11}NO_2$	PM	$^1H^b$	141

*indicates the study of polycrystalline compouds.
†indicates the study of single crystals.
‡denotes the liquid crystal.
LT denotes studies at low temperature.
The type of information is indicated by a, b, c and d, where 'a' refers to structural information, 'b' to the study of molecular motions, 'c' to the study of quadrupole effects, and 'd' to the study of water molecules in hydrated crystals.

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Burning Rate Modifiers for Composite Solid Propellants

GURDIP SINGH

Chemistry Department, Gorakhpur University, Gorakhpur 273 001

Ammonium perchloroate (AP) is the oxidiser and principal ingradient in most of the composite solid propellants. The deflagration rate of AP and composite solid propellants can be accelerated or suppressed by the addition of small amounts of various modifiers. The mechanism of action of these modifiers has not been elucidated clearly so far. Studies on the influence of modifiers on burning rate are helpful in understanding the mechanism of combustion and improving the theoretical models for combustion. The role of metal oxides in the decomposition of AP has been reviewed by Jacobs *et al.*[1]. The work reported on the role of catalysts in the composite propellants is meagre[2-6]. This article presents a comprehensive account of the role of modifiers (catalysts as well as inhibitors) in the decomposition and combustion of AP and composite solid propellants.

Importance of Modifiers

The modifiers are generally used for (i) the acceleration and deceleration of burning rates, (ii) improving chemical stability to avoid deterioration during storage, (iii) controling the radiation absorption properties, (iv) increasing the physical stregnth and decreasing the deformation, (v) suppressing the combustion instability, and (vi) minimizing the temperature sensitivity of the composite solid propellants. The temperature sensitivity has been found to be lowered from 0·5–1·0%°C to 0·2%°C for platonized propellants.

Combustion instability is a serious problem in solid propellant motor firings. Aluminium powder is largely used for overcoming this problem[7]. But Al powder contributes only to low frequency instability and there are propellants like double base propellants to which Al powder cannot be added readily. The use of modifiers in the conventional solid propellants has been found to be valuable in suppressing the combustion instability of rocket motors; a plateau is observed in the burning rate-pressure curves[8].

The addition of certain substances, notably metal oxides, such as oxides of Ca[9]; Al, Mn and Fe[9-10]; Ni, Cr and Co[11]; Sn[12] and Cu[13,14], has a marked effect on the decomposition of AP. The effect of silver, copper and iron perchlorates and ammonium iodide and bromide has also been investigated[15]. Solymosi[16] studied the effect of catalysts on the gas phase decomposition of AP. The deflagration of AP pellets containing copper chromite and carbon was investigated by Levy and Friedman[17]. Recently, Boggs *et al.*[18] measured the deflagration rate of AP in the presence of various inorganic additives; typical data are given in Table 1.

It has been observed that some catalysts, which activate AP decomposition, are rather poor burning rate catalysts. It seems that the data obtained for AP+modifiers would not be applicable to the deflagration of composite propellant+modifiers. In the presence of modifiers, the fuel-AP systems would exhibit entirely different characteristics compared

*Modifiers in this manuscript imply only positive catalysts or inhibitors

TABLE 1 — DEFLAGRATION RATE[18] OF AMMONIUM PERCHLORATE WITH VARIOUS MODIFIERS AT 1000 PSI

Modifier (additive)	Deflagration rate, cm/sec			
	$T_o = 26°C$		$T_o = 100°C$	
	2%	8%	2%	8%
Nil	0·35	0·35	0·38	0·38
CuO 202 (Harshaw)	0·41	0·46	0·68	0·78
Copper chromite catalyst (ROC/RIC)	—	0·20	0·41	0·55
Copper chromite catalyst (Alfa Chemicals)	—	0·26	0·61	0·69
Cupric oxide	—	0·25	—	0·58
Cuprous oxide	—	0·57	—	0·80
Chromic oxide	0·35	—	0·62	0·61
Ammonium chromate	0·40	0·50	0·52	0·70
Ammonium dichromate	0·42	0·58	0·42	0·52
Ferric oxide	0·49	0·1–0·15	0·63	0·4–0·5
Stannic oxide	DNB	DNB	0·10	DNB
Manganese dioxide	DNB	DNB	0·15–0·25	—
Titanium dioxide	DNB	DNB	0·15	—
Zinc oxide	DNB	DNB	DNB	DNB
Ammonium chloride	DNB	DNB	—	—
Ammonium sulphate	Negligible effect	Negligible effect	DNB	DNB
Ammonium bisulphate	DNB	0·35–0·40	DNB	DNB
Ammonium fluoride	DNB	DNB	DNB	DNB
Ammonium bifluoride	DNB	DNB	DNB	DNB
Ammonium oxalate	DNB	DNB	0·3–0·4	DNB
Ammonium acid phosphate	DNB	DNB	DNB	DNB
Potassium perchlorate	0·15–0·45	—	0·18–0·75	—
Potassium chloride	0·15–0·20 (at 0·5%)	0·11–0·25 (at 1%)	—	0·3–0·5 (at 1%)
Lithium perchlorate	0·3–0·5	—	0·7–0·8	—
Cadmium perchlorate	DNB	DNB	DNB	DNB
Copper perchlorate	DNB	DNB	—	—
Calcium oxalate	DNB	—	DNB	—
Lead chloride	DNB	DNB	DNB	DNB

DNB — Did not burn

with the uncatalyzed systems. Surface reactions (catalyzed or inhibited) would be expected to play an important part in both the ignition and combustion of composite propellants.

Burning Rate Catalysts

Copper chromite catalyst — The decomposition of mixtures of AP and various oxides of copper and chromium has been investigated extensively[19–23]. Hermoni and Salman[24] reported that catalysis took place in the solid phase, whereas Jacobs *et al.*[19] found that copper chromite altered the low temperature reaction slightly but accelerated the high temperature reaction. AP decomposes into NH_3 and $HClO_4$ and these molecules diffuse over the surface of the sample and are adsorbed by the catalyst. NH_3 is oxidized, whereas $HClO_4$ is decomposed further. Thus, copper chromite provides some additional surface on which NH_3 and $HClO_4$ get adsorbed, react and increase the forward reaction rate.

$$NH_4^+ClO_4^- \underset{\leftarrow}{\overset{\text{Catalyst}}{\rightarrow}} NH_3 + HClO_4$$

Friedman *et al.*[25] found that small quantities of a catalyst increase the low pressure deflagration limit (P_{dl}), while large amounts (10%) lower P_{dl} (15 atm). Glaskova[26] and Shadman-Yazdi *et al.*[27] reported the superiority of copper chromite in the accelerating action over other additives. Based on experimental observations, it was concluded[18] that (i) the burning rate of catalyzed AP was higher than that of pure AP, except for 8% copper chromite at 26°C and 1000 psi (Table 1), (ii) the temperature sensitivity of catalyzed AP decreased with increased in pressure, and (iii) the burning rate exponent (n) decreased with increase in the initial temperature of catalyzed AP. The concentration of the catalyst also affected the value of n as follows : (a) n increased at concentrations $<4\%$ and decreased at $>4\%$ (T_0, 26°C), (b) n increased at $<2\%$, remained constant for 2-6% (T_0,100°C) and decreased at $> 6\%$.

AP has been found[28–33] to burn with a liquid frothy surface layer at pressures below 800 psi; 70% energy transfer occurs in this layer[29,30]. The quantity of liquid decreases as the pressure is increased, giving ridges and valleys on the regressing surface. At

about 200 psi, purely gas phase controlled burning occurs. Boggs *et al.*[18] showed that burning rate at high pressure is constant at various concentrations of the catalyst. Hence, the copper chromite catalyst affects the condensed phase reactions and the effectiveness diminishes in the gas phase controlled reactions. The temperature sensitivity has also been found to decrease at higher pressure due to the fact that copper chromite alters the surface reactions. The low burning rate at higher concentration of the catalyst (Table 1) is due to the accumulation of the material on the regressing surface. The burning rate of polystyrene (PS)/AP propellants has been found to be enhanced by copper chromite[34].

Oxides of copper — Many workers[13,14,35,36] have reported that both CuO and Cu_2O catalyze AP decomposition. Jacobs and Kureishy[36], in addition, observed that CuO was a superior catalyst in comparison to both Cu_2O and copper chromite and that the high temperature decomposition of AP was enhanced considerably.

Shidlovskii *et al.*[37,38] and Bakhman *et al.*[39] showed that the addition of CuO or Cu_2O resulted in enhanced burning rate and stable combustion of AP at 1 atm (i.e. lowers the deflagration limit P_{dl}). These results are contradictory to the findings of Friedman *et al.*[25] who reported increase in P_{dl} (140 atm) when 3% CuO was added to AP. Shadman-Yazdi and Peterson[27] observed that small amounts (0·02–3·0 mole %) of CuO increased P_{dl}, while large amounts (>3.0 mole%) lowered the P_{dl} of AP. Schmidth *et al.*[40] also found that Cu_2O caused deflagration of AP between 245 and 260°C. But according to Boggs *et al.*[18], addition of CuO or Cu_2O to AP pellets did not sustain burning at most of the pressures. Addition of Cu_2O at 8% level is as effective as that of Harshaw CuO 202 at T_0=100°C (Table 1). However, CuO is not as effective as Cu_2O. Motion pictures of the burning surface of red pellets containing Cu_2O turned black. It is assumed to be due to the formation of CuO. CuO is found to be a superior catalyst for decomposition, whereas Cu_2O is better for deflagration of AP. All copper compounds are more effective in the case of condensed phase controlled reactions. Recently, Rastogi *et al.*[5] have reported that copper carbonate is a better catalyst in comparison to CuO in the combustion of polystyrene (PS)/AP propellants.

Copper chromate — Pearson[41] examined the thermal decomposition of copper chromate and chromite by TGA and DTA to understand the mechanism of their action. The successive stages in the decomposition of both these compounds have been found to be identical at higher temperatures and both yield Cu_2O ultimately as, shown below :

$$\text{Copper chromate} \xrightarrow{450^\circ\text{-}510^\circ\text{C}} \text{Cupric chromite}$$

$$\text{Cupric chromite} \xrightarrow{900^\circ\text{C}} \text{Cuprous chromite}$$

$$\text{Cupric oxide} \xrightarrow{2100^\circ\text{C}} \text{Cuprous oxide}$$

Thus, it is not copper chromate which acts directly as a catalyst; it first gets converted to CuO or Cu_2O, which actually catalyzes the reaction. This is supported by the fact that the catalysts (copper chromite and chromate) are effective at temperatures close to the surface temperature of the propellant[42]. The reactants are first adsorbed on the surface of the catalyst, and then the reaction takes place followed by desorption from the surface. The excess heat released on the catalyst particles probably enhances the burning rate. These catalysts are also found to affect the reaction of $HClO_4$ with solid fuel[43].

Ferric oxide — Shidlovskii *et al.*[37,38] found that (i) the oxides of iron promoted the complete decomposition of AP at 270-280°C, (ii) the maximum rate of decomposition of the mixture of AP and Fe_2O_3 was lower than that of pure AP, and (iii) AP + Fe_2O_3 did not burn at 1 atm (T_0, 20° and 100°C). It was observed that the addition of Fe_2O_3 had little effect on the rate of decomposition of AP at 210-240°C, while at 245-270°C, the catalytic activity was enhanced significantly[44]. This is contrary to the observations of Solymosi and Dobo[45] who found that in the range 200-240°C, Fe_2O_3 lowered the induction period and increased the rate of decomposition of AP. Above 260°C, the decomposition became extremely rapid and resulted in an explosion. Friedman *et al.*[25] showed that 3% Fe_2O_3 increased P_{dl} and the burning rate was less than that in AP at low pressure (P<116 atm), but was higher at higher pressures. Shadman-Yazdi and Peterson[27] found that small amounts (0·1 mole%) of Fe_2O_3 increased P_{dl}, while large amounts lowered it. It has been observed[46] that iron and its compounds are not effective catalysts and there is no burning at 50-150 atm pressure.

Boggs and coworkers[18] reported that 2% Fe_2O_3 increased the deflagration rate and temperature sensitivity significantly over those of pure AP. Samples having 8% Fe_2O_3 (T_0, 26°C) displayed (i) lower burning rate, (ii) higher P_{dl} and higher slope for burning curves than for pure AP. At T_0=100°C and for 8% Fe_2O_3, the burning rate was virtually equal or slightly higher than that of pure AP (Table 1). These observations have been confirmed by other workers[25,27,46].

Chromium oxide — The decomposition of AP-chromium oxide mixture has been studied extensively[11,20,24,37,38,47,48]. Hermoni and Salman[11] advanced the idea that Cr_2O_3 catalyzed only the gas phase reactions. Solymosi *et al.*[48] reported that Cr_2O_3 catalyzed $HClO_4$ decomposition in the temperature range 180-300°C. Shidlovskii *et al.*[37,38] proved that AP having 5% Cr_2O_3 did not burn at atmospheric pressure (T_0, 20° and 100°C). Friedman *et al.*[25] found that addition of 3% Cr_2O_3 resulted in increase in P_{dl} to approximately 300 atm. Glaskova[26] reported that AP+3% Cr_2O_3 mixture did not burn up to 230 atm. Recently, Rastogi and coworkers[5] have reported that chromium carbonate is a better catalyst in comparison to Cr_2O_3 in the combustion of PS/AP propellants.

Numerous other catalysts have been used for composite propellants, but the precise mechanism of their action has not yet been established, since the studies were concerned more with the efficiencies

rather than with the mechanism by which they are effective.

Mechanism of Catalysis of AP Decomposition

Transition metal oxides catalyze the decomposition of AP as well as the oxidative degradation of high polymers. It appears that catalysts perform the function of enhancing the decomposition of both AP and the fuel binder. Undoubtedly, a combination of these two effects is required for understanding the role of burning rate catalysts in composite propellants. Thus, the catalytic action of these catalysts can be better understood by studying the decomposition of (i) AP, (ii) fuel binder, and (iii) propellant in their presence.

AP is stable at room temperature, but decomposes with a measurable rate at temperatures >150°C. Below 300°C, AP undergoes autocatalytic reaction of the type

$$\text{A (solid)} \longrightarrow \text{B (solid)} + \text{gas}$$

which ceases after about 30% decomposition. This is usually called low temperature decomposition (LTD). At temperatures above 350°C, high temperature decomposition (HTD) occurs. It has been observed that some catalysts affect LTD, some HTD and some both. It is also known that AP decomposes by the electron transfer process in the LTD region, whereas the proton transfer process is operative in the HTD region. Thus, various mechanisms of catalysis have been put forward which are discussed here.

Solymosi *et al.*[14,47] suggested that *p*-type metal oxides (MO) enhance catalytic decomposition of AP on account of their (oxides) increased electron hole density, as shown below :

$$\begin{aligned} ClO_4^- + MO^+ &\longrightarrow ClO_4 + MO \\ NH_4^+ + MO &\longrightarrow NH_4 + MO^+ \\ ClO_4 + NH_4 &\longrightarrow ClO_2 + 1/2\ N_2 + 2H_2O \end{aligned}$$

Thus, the formation of perchlorate radicals can be accelerated by *p*-type oxides, whereas *n*-type oxides cannot promote the formation of ClO_4 radicals.

The doping of the semiconductors supports the above picture[14,47,49]. It is known that in semiconductor oxides, electron and defect-electron concentrations can be increased or decreased by incorporating ions of different valencies. Thus, the catalytic decomposition of AP was found to increase with variation in the defect-electron densities of the *p*-type CuO[14] and Cr_2O_3[47,49].

A significant catalytic effect observed in the presence of *n*-type ZnO[12,20] and CdO[50] is contradictory to the above hypothesis. Detailed investigations have shown that the role of these oxides is different from those reported above. These oxides react with AP as follows :

$$2NH_4ClO_4 + MO \longrightarrow M(ClO_4)_2 + 2NH_3 + H_2O$$

It has been suggested that the formation of perchlorate salts was responsible for the observed acceleration of the reaction[50]. Patil *et al.*[51] suggested the formation of metal perchlorate ammines metathetically prior to ignition in the case of metal oxides and AP mixtures. It should, however, be noted that with low concentrations of the catalyst, the quantity of perchlorate salts/ammines formation is very small and still these are effective.

Recent investigations with pure AP have brought about a major change. The activation energies of LTD and HTD have been found to be identical, i.e., 30 kcal/mole. Mass spectrographic studies did not confirm the existence of the molecular complex. Therefore, the primary step in the decomposition of AP is the dissociation to ammonia and perchloric acid, i.e. AP decomposes by a proton transfer process.

For the decomposition of AP catalyzed by copper chromite, Jacobs *et al.*[19] suggested that $HClO_4$ formed during the dissociation of AP migrates to the surface of the oxide and there decomposes through a heterogeneous phase reaction. Since the dissociative vaporization of AP becomes more important at a higher temperature (>300°C), this reaction path seems quite plausible at least at higher temperatures. Further, the oxidation of NH_3 also plays a major role in the catalysis. However, Rastogi *et al.*[5] reported that the decomposition of AP increases due to some sort of catalyzed exothermic reactions when AP is heated with catalysts. It may be inferred that the effectiveness of oxides is due to (i) catalysis of the heterogeneous phase decomposition of $HClO_4$, and (ii) catalysis of the oxidation of ammonia. Those oxides which catalyze both the reactions can be considered most effective. Further, each reaction occurs on the surface of the catalyst, e.g. adsorbed ammonia is oxidised by radicals such as O, ClO, and ClO_2, which are formed by the decomposition of adsorbed $HClO_4$.

It has been pointed earlier that the oxidative degradation of the polymer is increased by catalysts. The mechanism of action of traces of metals, which catalyze the homolytic decomposition of hydroperoxides, may be expressed as follows[52]:

$$\begin{aligned} ROOH + M^+ &\longrightarrow RO\cdot + M^{++} + OH^- \\ ROOH + M^{2+} &\longrightarrow ROO\cdot + H^+ + M^+ \end{aligned}$$

This induced chain decomposition can be an important factor in accelerating the oxidative degradation of polymers.

Burning Rate Inhibitors

Ammonium salts — A number of ammonium salts have been used as burning rate modifiers. Recently, Boggs *et al.*[18] found that ammonium chromate and dichromate accelerated the burning rate, whereas ammonium orthophosphate, ammonium sulphate, ammonium bisulphate, ammonium chloride, ammonium fluoride, ammonium hydrogen fluoride and ammonium oxalate were burning rate inhibitors. The temperature senstivity of deflagration was also found to be higher than that of pure AP. Ammonium chromate and dichromate burn interestingly. High speed, high magnification motion pictures showed the formation of green snakes at the regressing surface. It has been reported that AP did not burn in the presence of 5% ammonium oxalate at 100 atm, while at 150 atm, the burning rate of the pellets was 33% faster than that of pure AP[53,54]. Small qtuanti-

ties of ammonium chloride lowered the burning rate and increased the flame temperature, whereas a stoichiometric mixture of 70% AP and 30% NH_4Cl could not be ignited[55]. These workers[54] suggested that endothermic dissociation of ammonium chloride lowers the temperature of the reaction layer in the condensed phase, causing lowering of the burning rate. The increase in flame temperature may be due to the oxidation of NH_3 produced by the sublimation of ammonium chloride.

It has been found that the addition of ammonium hydrogen phosphate suppresses the first exotherm of AP[56,57]. Rastogi *et al.*[5] also reported ammonium dichromate as a burning rate accelerator for PS/AP propellants.

Dioxides of manganese, tin and titanium and zinc oxide — These modifiers give conflicting results. Shidlovskii *et al.*[38] and Bircumshaw *et al.*[58] reported the accelerating effect of MnO_2 and found that P_{dl} is <1 atm with 5% MnO_2. Not much data are available on SnO_2. However, Solymosi[47] reported that SnO_2 catalyzed the decomposition of $HClO_4$ above 300°C. It has also been found that TiO_2 is completely inactive in the decomposition, whereas ZnO catalyzes the decomposition of AP[48]. Boggs *et al.*[18] reported that MnO_2, TiO_2 and SnO_2 lowered the deflagration rate of AP and pellets containing ZnO did not burn at all.

Perchlorates of lithium, potassium, zinc, cadmium and copper — Solymosi *et al.*[12] reported that zinc and cadmium perchlorates catalyzed the decomposition of AP, but Boggs *et al.*[18] found that pellets containing perchlorates of copper and cadmium did not burn. The deflagration of AP + potassium perchlorate (KP) fluctuates rapidly (Table 1). Many workers[46,59] have reported that AP and KP form solution (eutectic) and KCl is also produced at the regressing surface; the accumulated KCl causes fluctuations in the burning rate. This has been supported by the finding of Boggs *et al.*[18] that KCl lowers the deflagration rate when added to AP.

Glaskova *et al.*[54] found that LiF suppressed the burning rate of AP to about one-fifth of the original value; this was considered to be due to the formation of $LiClO_4$ as follows :

$$NH_4ClO_4 + LiF \longrightarrow LiClO_4 + NH_4F$$

$$NH_4F \longrightarrow NH_3 + HF$$

Markowitz and coworkers[60] have also reported that the melting point of AP + LiF sample was depressed via eutectic formation. On this analogy, a lower deflagration rate is expected with $LiClO_4$, but Boggs *et al.*[18] reported that it was not true (Table 1). The greatest enhancement was found to occur where the influence of AP melt was most pronounced. However, cinephoto micrography and scanning electron microscopy have indicated a rapid decomposition of AP containing $LiClO_4$. Recently, Glaskova[61] reported the inhibiting action of different types of additives and concluded as follows :

(i) Addition of 1% of salts of ammonia reduces the burning rate of AP by a factor of 3-4 at low pressure.

(ii) Halogenides of lead and cadmium have a similar effect.

(iii) A mixture of ammonium salts and halogenides of metals increases the inhibitins effect further.

Mechanism of Inhibition of AP Decomposition

The mechanism of action of inhibtors on the decomposition of AP has not been investigated so far. Carbonates of calcium, barium and strontium have been found to inhibit the decomposition of AP due to the formation of metal perchlorates[62]. This inhibition of decomposition of AP may be due to the higher stability of metal perchlorates in comparison to that of AP[63]. Gláskova[61] has suggested three possible ways of inhibition during the deflagration of AP + inhibitors : (i) Salts of ammonia decompose to liberate ammonia, which shifts the equilibrium of AP dissociation to the left, (ii) some additives bind $HClO_4$ and /or AP to less reactive compounds, and (iii) some substance inhibit the decomposition of $HClO_4$. However, it should be noted that dissociation equilibria of AP would hardly be affected, since a considerable inhibiting action was observed when the inhibitor concentration was only 1%. Similarly, the effect of metal perchlorate formation would also be marginal. The third explanation seems quite attractive, but more research is needed to confirm it. The inhibition of polymer degradation may also be due to the formation of non-radicals or inert products when polymers are heated with inhibitors[62].

Role of Modifiers in the Combustion of Composite Propellants

The acceleration or inhibition of the burning of composite propellants by modifiers may be due to (i) the competitive adsorption of reactants and products on the modifier surface, (ii) intermediate compound formation with AP + modifiers, (iii) products of decomposition of modifiers, (iv) catalyzed/inhibited condensed phase reactions, and (v) endothermic/exothermic decomposition of AP + modifiers.

It is generally considered that adsorption of the reactants occurs on the surface of the catalysts followed by the reaction and desorption. Accordingly, if the products are adsorbed more strongly than the reactants, the catalytic activity of the catalyst would be inhibited and the burning rate would be reduced. But the experimental proofs in this regard are still wanting. Studies in this area would be of considerable importance for improving the combustion processes.

As the decomposition of AP is catalyzed or inhibited through the formation of intermediate compounds, their formation on or beneath the propellant surface during deflagration may be possible, because the surface temperature of the propellants is of the order of 1000°C.

Analytical tests on modifiers have shown that they decompose during the combustion of propellants or AP and the residue accumulates on the burning surface in the form of fused mass, which further affects the combustion behaviour. It has also been observed that those modifiers (e.g. NH_4Cl, NH_4F, ammonium oxalate, ammonium hydrogen fluoride, etc.) which liberate NH_3 on decomposition at higher

temperatures, lower the burning rate through the common ion effect.

During deflagration of AP or propellants, a number of physical and chemical changes occur. The process begins with endothermic changes which produce intermediate gaseous products and ends with exothermic processes which produce the final products. The usual combustion models consider the gasification process as an edothermic step and the subsequent gas phase reactions as an exothermic step. However, some authors[64–67] have established the occurrence of exothermic reactions in condensed phase too. Recently, Korobeinchev *et al.*[68] on the basis of kinetic and thermal decompositions of AP–PS—Fe_2O_3 systems have concluded that decomposition is a multistage process involving reactions of $HClO_4$ with PS and condensed products. In steady deflagration, heat from the exothermic reactions is fed back to the condensed phase to maintain the exothermic step. A part of the heat is also lost by a different mechanism of heat transfer to the surroundings. This heat loss is usually assumed to become important close to the pressure limit and is considered by some to be the cause of extinction.

Modifiers probably affect most of these combustion steps, i.e. the endothermic and exothermic reactions and the heat losses. A combustion model should have the capacity to explain the actual effects of modifiers. Recently, Rastogi *et al.*[5,62] have shown that burning rate, surface temperature, flame temperature and rate of decomposition are enhanced in the case of catalyzed propellants, and lowered in the case of mixtures of propellant and inhibitor. This may be due to the heat produced in catalytic reactions in the former case; the burning rate is reduced on account of endothermicity of the condensed phase reactions on the propellant surface. It has also been reported[5] that carbonates of copper and chromium are better catalysts than their oxides. It is suggested that the former type of catalysts are ultimately converted to their oxides with finer particle size at the propellant surface. The freshly prepared and finer oxides contain a large number of defects and dislocations, providing active sites for adsorption and causing acceleration in the rate of reaction. It seems that the role of catalysts can be better understood by following the adsorption theory. The following are some of the requirements for positive catalysts: (1) Finer particle size having large number of defects and dislocations in the crystal lattice, and (ii) good adsorption capacity and large surface area. However, a great deal of work is required to be undertaken for understanding the role of modifiers.

Summary

The role of burning rate modifiers in the decomposition and combustion of ammonium perchlorate and composite propellants is reviewed. Some important modifiers are discussed and the possible mechanism of their action is suggested. Emphasis is laid on the adsorption and intermediate compound formation theories which seem to be important for understanding the role of modifiers in composite propellants.

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The Quaternary Structure of Glycoprotein Hormones—Recent Developments

M. R. SAIRAM

Reproduction Research Laboratory, Clinical Research Institute of Montreal, Montreal, Quebec H2W 1R7, Canada

I. Introduction

UNTIL recently, progress in the characterization of the glycoprotein hormones, in general, lagged behind the major advances achieved with the simple peptide and protein hormones of the pituitary. Several factors such as the low content of these hormones, their relatively low stability, problems in isolation and heterogeneity arising out of polymorphism have contributed to this slow progress. However, within the last seven years, spectacular advances revealing a wealth of information on the glycoprotein hormones have been made. The new concept of subunit structure of these hormones has been brought into the picture and within a short span of about five years. remarkable structural similarities in the organization of the glycoprotein hormones have been revealed.

The glycoprotein hormones are the only class of hormones which have a true subunit structure. These hormones consist of two non-identical polypeptide chains, designated α and β, which are associated together by non-covalent bonds. Disruption of the quaternary structure generally results in the loss of much of the biological activity of the original hormone. Recombination of the subunits leads to, in many cases, partial or, in some cases, complete restoration of the biological activity. Structural investigations have led to the recognition that, within a species, the amino acid sequence of the α-subunit is virtually identical. This subunit is referred to as the common subunit. The β-subunits are different in structure and confer hormonal specificity to the complex. There must be subtle differences in their tertiary structure to account for the difference in the biological properties. The amino acid sequence information of the glycoprotein hormones is restricted to only a few species. Structures for the subunits of ICSH* from four species, TSH of bovine and human have been deduced. Preliminary data are available on human pituitary FSH. There is clearly a need for detailed studies on other species. Despite these limitations, certain structural features of the gonadotropins and thyrotropin can be recognized. The amino acid sequence of subunits of HCG has been established, while similar data are completely lacking for PMSG. There is virtually no information about the arrangement of mono-saccharides in the glycoprotein hormones, except perhaps for HCG. Tentative assignment of the carbohydrate sequence of HCG has been reported. The data on the prosthetic groups of the pituitary ICSH, TSH and FSH can only be regarded as preliminary; in most cases, this information is restricted to the number of residues of different monosaccharides present. The role played by the carbohydrate moiety has remained unclear. Where sialic acid has been found in the hormone, it has been shown to influence the circulating half-life in the blood. This acidic sugar confers a protective role on the molecule from metabolic degradation.

The glycoprotein hormones are generally excellent antigens; thus, antibodies can be raised to most of them after injection into a suitable animal. In many cases, most of the antigenic determinants of the molecule have been found on the β-subunit. In contrast, the α-subunit is a weak antigen.

A simple model of the glycoprotein hormones is depicted in Fig. 1. The basis for representing them as such is discussed in this article. This review is confined to the advances made mainly in the last 5 years. The reader is referred to other sources for detailed descriptions[1–4]. Although the human urinary gonadotropins have been in the picture for several decades now, convincing data on their chemistry are yet to come. Hence, these are not included in the present discussion.

II. Some Characteristics of the Glycoprotein Hormones

Highly purified preparations of pituitary ICSH, TSH and FSH have been obtained from several species[2,3]. HCG has been isolated from commercial preparations of crude material obtained from the urine

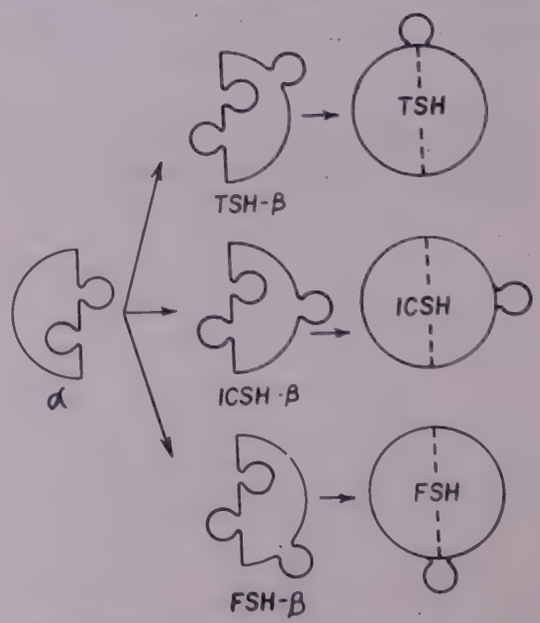

Fig. 1 — Schematic representation of the quaternary structure of ICSH, FSH and TSH [A nearly identical α-subunit combines with a specific β-subunit to give rise to a molecule with distinctly different biological properties. The diagram implies that the contact or binding sites of the β-subunit must either be identical or nearly so for combination with the α. A conformational change occurs upon association of the two subunits]

*Abbreviations used: ICSH, interstitial cell stimulating hormone (luteinizing hormone — LH); FSH, follicle stimulating hormone; TSH, thyroid stimulating hormone; HCG, human chorionic gonadotropin; PMSG, pregnant mare serum gonadotropin; The IUPAC-IUB Commission on Biochemical Nomenclature Recommendations has suggested the names lutropin, follitropin and thyrotropin for pituitary ICSH (LH), FSH and TSH respectively [*J. biol. Chem.*, **250** (1975), 3215]. The literature cited in this article is rather selective. For a better access, the reviews cited may be consulted.

of pregnant women[4]. Similarly, PMSG can also be obtained in highly purified form starting from commercial preparations of pregnant mare serum[5,6]. In general, all these hormones have been difficult to purify and despite the advances in techniques of protein purification, efficient methods for the purification of FSH and TSH are still not available. FSH continues to be the most difficult to obtain in sufficient quantities for chemical studies. Several factors seem to be responsible for this. The high lability of FSH has been a significant factor in reducing the yields and polymorphism also appears to have been responsible.

Some properties of the well-characterized glycoprotein hormones are listed in Table 1. In general, the 3 pituitary hormones have a molecular weight of approximately 30,000. The placental gonadotropins HCG and PMSG are slightly larger in size with molecular weights of 38,000 and 52,000 respectively.

It is evident from Table 1 that the sedimentation coefficient of these hormones is markedly dependent on the *p*H of the medium employed, the value being generally higher in alkaline and lower in acidic solutions. This was first recognized for ovine ICSH by Li and Starman[7] in 1964 who observed a decline in $S_{20,w}$ value of 2-74 S to 1·64 S for a change in *p*H value of the medium employed from 8·4 to 1·3. Since an $S_{20,w}$ value of 1·64 S corresponds to a molecular weight of 16,000, it is concluded that ovine ICSH exists as a monomer of 16,000 in acidic solutions. This was a key observation that provided a strong impetus to the later discovery of the quaternary structure of ovine ICSH followed by other glycoprotein hormones (*see* Section on Subunit structure). There are certain exceptions to this general pattern, as illustrated by the behaviour of bovine TSH, which did not show a reduction in molecular weight, unless examined under unusual dissociating conditions, such as 1·0 *M* propionic acid[3]. This could be interpreted as being due to the stronger subunit interactions in this hormone[3]. However, since bovine TSH did not behave like ICSH under dissociating conditions, the

TABLE 1 — SOME CHARACTERISTICS OF GLYCOPROTEIN HORMONES

Hormone	Mol. wt	$S_{20,w}$	No. of residues	Carbohydrate %	No. of subunits	Terminal residues	
						—NH_2	—COOH
Lutropin							
Human	29,120*	2·71 (*p*H 3·6) 1·57 (*p*H 1·2)	204	23·1	2	Val,Ser	Ser,Gly
Ovine	28,300*	2·74 (*p*H 8·4) 1·64 (*p*H 1·3)	215	14·3	2	Phe,Ser	Ser,Leu
Bovine	28,300*	2·67 (*p*H 8·4) 1·66 (*p*H 1·3)	215	13·0	2	Phe,Ser	Ser†,Leu
Porcine	27–34,000	2·46 (*p*H 6·5) 2·09 (*p*H 1·0)	209	14	2	Thr,Ser	Ser†,Leu
Equine	34,000			24	2		
Rat	31,000			14·7	2		
Thyrotropin							
Human	28,900*	2·84 (*p*H 8·2) 2·01 (*p*H 1·5)	201	16·2	2	Val,Phe	Ser,Tyr
Bovine	28,300*	2·76 (*p*H 5·35) 2·76 (*p*H 1·15)	209	12	2	Phe	Ser,Met
Follitropin							
Human	31,000	2·89 (*p*H 7·0) 0·61 (8*M* urea *p*H 7·0)	207	25·9	2	Ala† (Val)	Set†
Ovine	31,000	2·63 (*p*H 5·0) 1·54 (*p*H 1·3)		14–20	2		
Equine	33,800			24·3	2		
HCG	37,900*	2·89 (*p*H 5·5)	239	30·8	2	Val,Ser	Ser,Pro
PMSG‡	52,000			45·0	2		

*Values derived from actual sequence data.

†There is uncertainty about the presence of a free terminal serine in bovine ICSH β. It is believed to be partially free by one group, while the other claims that it is blocked. The porcine β is reported to have a blocked serine. In human FSH the report of Rathnam and Saxena[76] shows Ala at the $-NH_2-$ terminus of α, while Shome and Parlow[77] indicate Val. Discrepancy is due to microheterogeneity (*see* text for details). The COOH terminal residues in human FSH β have not been determined in the preliminary sequence report[78].

‡Data available are incomplete.

similarity in the structural organization (quaternary structural features) remained unrecognized until the final stages of studies on the structure of TSH.

The carbohydrate moiety is covalently linked to the polypeptide chain. The placental gonadotropins have nearly twice (30% or more) as much carbohydrate as the pituitary FSH, ICSH and TSH. The sugars found in all the glycoproteins are mannose, galactose, fucose, galactosamine, glucosamine and sialic acid. The amino sugars have been shown to be N-acetylated in ovine ICSH[8]. This might be true in the case of other hormones also, but it remains to be established. A major difference in the oligosaccharide moiety is the presence of sialic acid in certain molecules. The placental HCG and PMSG contain a high proportion (10%) of sialic acid. The presence of this charged sugar residue could explain the low isoelectric point of these two hormones. This sugar is present in human pituitary ICSH, TSH and FSH. In bovine TSH and ICSH, little or no sialic acid is found. Equine ICSH and FSH have nearly as much sialic acid as the placental gonadotropins. The physiological significance of this highly acidic sugar in these hormones is not completely clear. Enzymatic removal of sialic acid by neuraminidase treatment inactivates the molecule, as determined by *in vivo* assays. However, the biological activity is retained in *in vitro* assay systems[9]. The available evidence indicates that sialic acid plays a major role in determining the survival of the molecule in circulation[10,11], the liver rapidly eliminating the desialylated molecules. It is also known that sialoproteins are generally more resistant to proteolytic attack.

The total number of amino acid residues, as is presently known from the structural data on several hormones, is in the range 201-239. It is most probable that hormones of other species will have approximately the same size of polypeptide chain. It has now been firmly established that all the glycoprotein hormones have two non-covalently linked subunits and thus possess a quaternary structure (*see* later sections for details). Accordingly, two N-terminal and two C-terminal amino acids are found in each molecule. It has been reported that the amino terminal of the β-subunit in some hormones is at least partially acylated[12,13]. However, this has remained a point of controversy between several laboratories[12,14].

III. Amino Acid Composition and Polymorphic Nature

The amino acid composition of human pituitary ICSH, FSH and TSH, as computed from the recent structural data (Fig. 2), has shown that the three hormones are identical to one another in respect of the number of cystine residues present in them, but show variance with regard to the tryptophan, proline and tyrosine residues. While the composition of ICSH is significantly different from the other two hormones, the differences between the latter two are not very prominent. The total number of amino acid residues in the three hormones is approximately the same. The composition of HCG (not shown) resembles that of ICSH in many respects.

One of the major persistent problems in the isolation of gonadotropins and TSH from different species has been the polymorphic nature or the electrophoretic heterogeneity frequently encountered in the highly purified preparations (*see* refs. 2,3). Looking at it in retrospect, we might say that this was to a certain extent a hindrance to an assault on their structural determination.

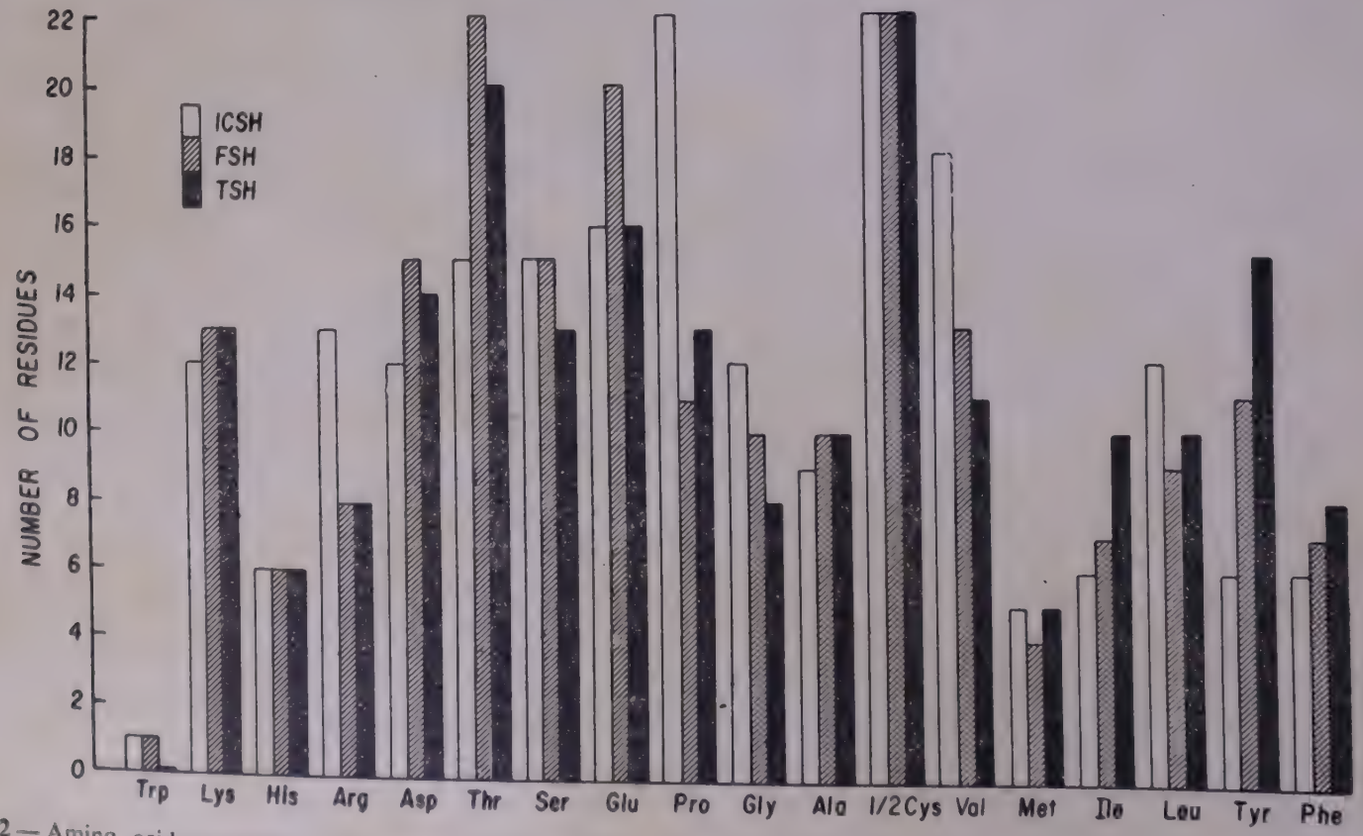

Fig. 2 — Amino acid composition of human pituitary ICSH, FSH and TSH as computed from their primary structures [From refs. 66, 67 (ICSH); 76, 77 (FSH); 39, 71 (TSH)]

Numerous reports dwell on the multiplicity of components in all the hormones from different species. These different components have been, in some cases, isolated in small quantity by tedious and laborious procedures. In most cases, no major differences were detected in amino acid composition (within experimental error), but slight differences in carbohydrate content were revealed. In some cases, the biological potencies of the different components vary significantly. The heterogeneity and hence the variations in the biological activities of the various fractions obtained during purification of HCG have been ascribed to the presence of varying amounts of sialic acid[15].

An adequate explanation of the basis of polymorphism might be rather difficult. However, several facts became apparent during detailed structural studies on ovine ICSH and bovine TSH subunits. The existence of heterogeneity at the termini might be a result of proteolytic degradation either during isolation or storage of the tissue itself. Differences in carbohydrate content could arise because of the action of carbohydrases or an incomplete biosynthesis during the post-transcriptional events. Amide differences could also contribute to heterogeneity. In addition, polymorphism could arise as a result of small conformational differences. Last but not least is the fact that genetic factors could be involved in the polymorphic behaviour of some of these hormones, although this is difficult to prove.

IV. Biological Activity

The gonadotropins stimulate the ovary and testes to secrete steroids. TSH, on the other hand, stimulates the thyroid to secrete thyroxine. Until recently, for all these hormones, only the conventional *in vivo* bioassay systems were available[2,3]. Now, rapid and simpler *in vitro* assay systems involving the use of isolated cells have become available for ICSH[16–18] and FSH[19]. In addition, radioreceptor assays have come into vogue. These rely on the specificity of the hormone receptors in target tissues[20] and competition between the cold and labelled hormone. HCG resembles pituitary ICSH in its biological actions. PMSG resembles pituitary FSH in activity, but it also has significant ICSH activity. In this respect, it can be regarded as a hybrid molecule.

TABLE 2 — BIOLOGICAL ACTIVITIES OF GLYCOPROTEIN HORMONES*

	Human	Ovine	Bovine	Porcine	Equine	Rat
ICSH	3·0–10·7	1·9–4·5	1·5–1·9	0·7–0·8	5·3	1·2–1·7
TSH	7–20		30–50	35		
FSH	428	133			90	

*The activities are usually expresssed in the different coventional assays in terms of a standard usually supplied by the US National Institutes of Health, Bethesda. For some details of assays and sources of the values shown in this table, *see* reference 2 (for ICSH and FSH) and reference 3 (for TSH). TSH potencies are usually expresssed in terms of an international standard.

The biological potencies of some of these hormones are listed in Table 2. In ICSH and FSH, the human hormone is the most active of those isolated in a highly purified state. In TSH, the best and the highest recorded activity has been noted for the bovine hormone. One of the general features of the glycoprotein hormones is their polymorphic nature. On careful analytical evaluation even the highly purified preparations have been shown to be electrophoretically heterogeneous and different biological activities have been recorded for the various components. Structural analysis has partly explained the multiplicity of components in these preparations (*see* later sections). As is true of many highly purified proteins, some of the glycoprotein hormones, especially FSH and TSH, show a tendency to lose biological activity on storage; ICSH, however, is remarkably stable.

V. Subunit Structure

Urea solutions at a high concentration are known to alter the structure and activity of proteins by disrupting the non-covalent interactions, such as H bonds. It was first reported in 1961 that ovine ICSH is inactivated by 6 *M* urea[21]. The dissociating effect of acidic solutions on ovine ICSH was observed in 1964 by Li and Starman[7] who suggested that the hormone consisted of monomeric molecules with a molecular weight of 16,000. This observation gave impetus to the study of the structure of ovine ICSH. It also provided a clue to the mechanism of inactivation of the hormone in acidic solutions. These observations were confirmed by Ward and Arnott[22] who investigated the behaviour of the hormone on ultracentrifugation and gel filtration in acidic media. These findings indicate that, under certain conditions, the ovine ICSH molecule (molecular weight 30,000) dissociates into smaller units of equal size. de la Llosa *et al.*[23] showed that ovine ICSH was dissociated by urea, guanidine hydrochloride and at *p*H below 3 into two subunits of approximately equal size (16,000). Upon removal of urea, the reassociation occurred under certain conditions with regeneration of biological activity[23]. The mixture of dissociated subunits possessed only about 9% of the original activity. The inactivation of the hormone in the presence of guanidine hydrochloride or at extremes of *p*H such as below 3 or above 12 was also explained on the basis of the dissociation phenomenon[24].

Unequivocal proof of the presence of a subunit structure in a protein depends upon their isolation and characterization. This was successfully achieved first for ovine ICSH by Papkoff and Samy who devised a method for the separation of subunits[25]. This was effected by subjecting the hormone to nine transfers in countercurrent distribution in the solvent system 40% ammonium sulphate-0·2% (dichloroacetic acid-*n*-propanol-ethanol (60:60:27:33). One of the subunits (designated CI) has a low partition coefficient and thus remains in the lower aqueous phase, whereas the other component (CII) having a high partition coefficient readily migrates to the upper organic phase. The amino acid composition of the two components was different, showing that the polypeptide chains were non-identical. The isolated subunits

had low biological activity, which was partially regained after reassociation under suitable conditions.

The existence of two non-identical polypeptide chains has been confirmed for ICSH from bovine[26,27], human[28,29], porcine[30], equine[31] and murine[32] pituitaries by the isolation of the two chains. In all cases, the dissimilar nature of the two chains became evident from amino acid composition alone. After the conclusive demonstration of subunit structure of ICSH, the observations were extended to FSH. The subunits of this hormone have been isolated from ovine[33,34], human[35] and equine species[36].

The subunit nature of TSH (bovine) was much difficult to demonstrate. In fact, its subunit nature did not become evident until the amino acid sequence studies of the hormone were well under way[3]. The data derived from experiments under a variety of dissociating conditions were in accord with a single peptide chain for bovine TSH. Unequivocal recognition of the true subunit nature of bovine TSH became apparent under a very unusual combination of dissociating conditions and fractionation of the two resulting components under another[37]. The hormone was first dissociated in 1 *M* propionic acid and lyophilized. Fractionation of the two subunits, though they are of equal size, was effected on Sephadex G-100 in NH_4HCO_3 because of differential interaction of the two subunits with the gel matrix. Human[38,39] and porcine[40] TSH have also been shown to consist of subunits.

The placental gonadotropins HCG and PMSG have also been shown to consist of two polypeptide chains. Methods have been devised for the separation of the subunits of HCG[41,42] and PMSG[43].

(a) *Nomenclature of the subunits* — As discussed above, all the glycoprotein hormones have now been shown to consist of two non-identical polypeptide chains. Although in some cases definitive information is restricted to only a few species, it is reasonable to expect the same general chemical make up for all mammalian hormones at least. It, however, remains to be seen if these structural features will be found in the lower species also.

In the initial stages of the investigations on the various glycoprotein hormones, different designations were given to the two polypeptide chains of the different hormones by various laboratories. The recognition of the close similarities in the structures has now led to a less confusing and uniform nomenclature. The two subunits of all these hormones are now designated α and β. Within a species, αsubunit is common to all the three pituitary hormones, ICSH, FSH and TSH, the β-subunit being different in each and specific for each hormone (*see* later sections). This designation is also convenient in specifying the subunits of different hormones from various species. For instance, ovine ICSH-α and human ICSH-β will be written as ICSH-α_o and ICSH-β_h respectively.

(b) *Separation of subunits* — The methods currently in use for the separation of the subunits of the glycoprotein hormones, viz. countercurrent distribution (CCD), ion-exchange chromatography following urea dissociation, salt precipitation and propionic acid treatment, involve preliminary dissociation of the hormone followed by a fractionation procedure to isolate the subunits. Because of the differences in the forces of interaction among the subunits and their properties, no single method is applicable to all the hormones. Thus, for example, while CCD method works well for ovine and bovine ICSH, it works rather capriciously with the human hormone. The same method, however, under slightly different conditions, works well for human TSH. Another widely employed method for the various hormones involves preliminary dissociation in 8 *M* urea followed by chromatography on ion-exchange Sephadex. A chemical modification method has also been utilized (example: ovine ICSH), but it is obviously of no value in the investigation of biological activity.

The simplest method described so far is the recent procedure of Sairam and Li[44]. In this method, ovine and bovine ICSH are first dissociated in acidic solutions at *p*H 3·5 and the β-subunit is salted out by 3*M* NaCl. The α-subunit remains in solution. Further purification of the subunits is achieved by

Fig. 3— Disc electrophoresis of ovine ICSH, β- and α-subunits (100 μg each) [7% acrylamide β-alanine acetate (*p*H 4·5) 4 mA/tube, 1 hr]

gel filtration. The yield of the subunits is much higher than that obtained by the CCD method and so is the quality of the subunits. The high purity and electrophoretic differences of these subunits and their comparison with the native hormone are shown in Fig. 3. Full biological activity is restored upon recombination[16]. For proteins having a quaternary structure, the best evidence of the preservation of native structure during isolation is the complete restoration of biological properties after recombination. In this respect, only the subunits of ovine and bovine ICSH isolated by the new method of salt precipitation meet this criterion. ICSH subunits prepared by other methods yield a recombinant with lower biological activity and consistent complete restoration of activity has not yet been attained with any other hormone.

(c) *Biological properties of subunits* — The biological activity of the isolated subunits of these glycoprotein hormones is an interesting aspect of the study. It was mentioned earlier that most of the biological activity of ICSH was lost upon dissociation of the hormone. Many studies show that the isolated ICSH subunits have little, if any, biological activity[45], either in the *in vivo* OAAD* assay[46] or in the *in vitro* Leydig cell assay[16]. Highly purified ICSH subunits exhibit less than 0·2% activity of the native hormone[16]. Similar observations have been made with the subunits of HCG[47], bovine TSH[37], human TSH (M.R. Sairam, unpublished data), porcine TSH[40], human FSH[35] and ovine FSH[34].

It cannot be stated categorically, on the basis of the conventional assays alone, that the subunits of ICSH, FSH, TSH or HCG do not have any biological activity. Significant biological activity has indeed been detected for the various subunits in certain other assay systems. However, in such studies, the chemical purity of the isolated subunits (especially for contamination with the native hormone or the counterpart subunit) must be carefully evaluated. It has been found that[48] while ovine ICSH-α (CCD)† is inactive in the *in vitro* lactic acid production from ovaries, the β-subunit (CCD) retains about 25% of the activity as compared to the native hormone. Approximately the same degree of activity (25%) was found by Yang *et al.*[49] for the ovine ICSH-β subunit (CCD) in the induction of ovulation in hamsters. They have also shown that ovine ICSH-β (CCD) is also capable of maintaining pregnancy in rats hypophysectomized on the 8th day of pregnancy[50]. Gospodarowicz[51] has reported that, in the mouse adipose tissue, ovine ICSH-α (CCD) has as much lipolytic activity as the native hormone, while ICSH-β (CCD) is totally inactive. Farmer *et al.*[52], however, found that in a similar assay in rats, both subunits did not exhibit any significant biological activity. Ovine ICSH-β (CCD) was found to bind to rat ovaries under various physiological states, although not always with the same avidity as the native hormone[53]. In these systems ICSH-β cannot increase cyclic AMP levels, although ICSH can do so. Thus, the binding of a molecule need not necessarily reflect its biological activity.

The isolated subunits of ovine ICSH and HCG were found to block the stimulatory action of the intact hormones on the formation of 5′-phosphoribosylglycinamide[54]. This is one of the early steps of purine nucleotide biosynthesis *de novo* in the high speed supernatant fraction from the corpus luteum of the ovary. It has been suggested that the corpus luteum glucose-6-phosphate dehydrogenase is under allosteric regulation by ICSH and the isolated subunits compete with the hormone for the regulatory site on the enzyme[55]. This implies that the hormone and subunits are capable of entering the cell.

In a non-mammalian system, the lizard *Anolis carolinensis*, the activity of ovine FSH can be fully accounted for solely by the FSH β-subunit[56]. Highly purified preparations of HCG subunits apparently increase cyclic GMP levels in luteinized ovaries, while the intact hormone does not[57]. An elevation of plasma progesterone level in the pseudopregnant rat occurred with HCG and its subunits. Cyclic GMP has been implicated as a possible intracellular mediator in the steroidogenesis induced by the subunits[57]. In the rabbit, *in vivo* studies indicate that the isolated ovine ICSH subunits do influence steroid secretions, but the profiles are different from that elicited by the intact hormone[58].

Both the α- and β-subunits of bovine TSH are reported to bind to bovine thyroid plasma membranes, whereas only the β-subunit inhibits the binding of tritiated TSH[59]. However, Lissitzky *et al.*[60] attributed this to contamination of the subunits by the native hormone. The binding of TSH-β is associated with considerable biological activity, such as adenylate cyclase activation, glucose oxidation or colloid droplet formation; the level of activity is, however, much lower than that of the native hormone[61].

It is extremely difficult to assess whether the low level of activity is because of intrinsic activity or whether it is a result of minute contamination. However, the various observations cited above, although difficult to reconcile with the current concepts of hormone action, cannot be ignored. Perhaps, the final unequivocal answer has to await the total laboratory synthesis of the individual subunits or fragments.

(d) *Biological properties of recombinants* — The isolated subunits of the glycoprotein hormones are biologically inactive in the conventional bioassays. A combination of the α- and β-subunits is essential for the generation of biological activity. The degree of recovery of activity has been reported to vary in the range 20-100%. Such wide variations in the recoverable activity appear to be related partly to the method of subunit isolation and partly to the incomplete understanding of the conditions for proper recombination of the subunits.

The first demonstration of the subunit nature of ovine ICSH greatly influenced work on the other glycoprotein hormones and led to the identification of their subunits. When the two non-identical hormone subunits α and β were available, it became evident that the α-subunit could be used interchangeably to gene-

†OAAD assay, ovarian ascorbic acid depletion assay. (This is an *in vivo* assay for ICSH, widely employed until recently).

†Subunits prepared by the countercurrent distribution method (CCD).

rate a complex with biological activity. The first few experiments in the generation of hybrids were conducted with bovine ICSH and bovine TSH subunits[37]. The interchangeability of ICSH α and TSH α provided the first indication that the three-dimensional structures of at least one-half of the hormone molecules, namely the α-subunit, must be very similar. This has been corroborated by detailed structural analysis (*see* Section on chemistry), which has been extended to many other species. Some examples of the biological activity of the various hybrids are given in Table 3. It can be concluded from these data that a hybrid combination of the β-subunit of one hormone with the α-subunit derived from any other hormone gives rise to a product which has biological activity of the hormone from which the β-subunit was derived. In other words, the β-subunit of the hormone may be designated as the hormone specific, while the α-subunit can be termed the common subunit. For example, a hybrid of human ICSH α+ human FSH β generates FSH activity, while a hybrid of human FSH α + human ICSH β will have ICSH activity. In addition, interspecies hybrids can also be made with generation of at least partial activity or in some cases even greater activity than the native hormone itself.

It is of particular interest to draw attention to the biological activity of hybrids generated using the subunits of HCG (Table 3). The hybrid HCG α + bovine ICSH β has twice the activity of native bovine ICSH itself or the homologous recombinant bovine ICSH α + bovine ICSH β. It is probable that the higher activity observed for this hybrid involving HCG α is a reflection of the longer half-life due to the presence of sialic acid in HCG α[62]. It can also be attributed to greater affinity of the hybrid to the receptor; this seems possible because in *in vitro* assays the consideration of half-life is largely, if not entirely, eliminated.

A truly intriguing and fascinating question arises as to the role of the α-subunit in the expression of biological activity of hormone. Since the α-subunits have been shown to be interchangeable, it cannot be assumed that they just serve to induce the orientation of the β-subunit in such a way as to favour its interaction with the receptor at the target tissue. In recent experiments (M.R. Sairam, unpublished data), it has been observed that while, in an *in vitro* lipolysis assay, the homologous recombinant human TSH α + human TSH β is fully active, the hybrid of human ICSH α + human TSH β shows considerably low activity, indicating that the α-subunit might be more important in imparting biological activity to the homologous complex than has been recognized so far. The human TSH α- and β-subunits and the human ICSH are inactive in this *in vitro* assay. More rigorous studies with subunits of hormones prepared by milder methods are necessary, which will throw more light on the role of the two subunits and also might amplify the significance of the subtle differences noted in the α-subunit (for example within a species).

Table 3 — Biological Activities of Subunits, Recombined Molecules and Hybrids*
(Data given are very selective)

Hormone/Hybrid	Activity†			
	ICSH	FSH	TSH	Ref.
Human ICSH	8·8			28
Human FSH		185		
HCG	19·9			
ICSH-α_h+ICSH-β_h	3·8			
FSH-α_h+ICSH-β_h	4·6			
FSH-α_h+HCG-β	18·0			
HCG-α+ICSH-β_h	6·9			
ICSH-α_h+HCG-β	7·9			
ICSH-α_h+FSH-β_h	1·2	22·6		
FSH-α_h+FSH-β_h		50·0		
HCG-α+HCG-β	16·0			
HCG-α+FSH-β_h	0·8	53·4		
Bovine ICSH	2·2–2·9			37,109
Bovine TSH			30–40	
ICSH-α_b+ICSH-β_b	2·6			
ICSH-α_b+TSH-β_b			+ve	
ICSH-α_b+HCG-β	5·4			
TSH-α_b+ICSH-β_b	0·94			
HCG-α+ICSH-β_b	4·9			
TSH-α_b+HCG-β	3·3			
PMSG†	100	100		43
PMSG-α	3·6	2·5		
PMSG-β	6·2	5·0		
PMSG-α+PMSG-β	31·5	43·6		
PMSG-α+ICSH-β_o	20·6			
PMSG-α+FSH-β_o		16·0		
ICSH-α_o+PMSG-β	7·0(N.S.)			
PMSG-α+HCG-β	33·2			
HCG-α+PMSG-β	5·1(N.S.)			

*Hybrid molecules are generated by incubation of an α-subunit from one hormone with the β-subunit of another. Conditions employed vary (*see* references for details).

†Activity is usually expressed as units/mg (ICSH and FSH) in terms of standards supplied by the US National Institutes of Health. TSH activity is expressed in terms of an international standard.

‡The activity of native PMSG is taken as 100% and all other values are expressed in terms of this; NS denotes not significant.

VI. Primary Structure of the Hormones

(a) *Amino acid composition* — The amino acid compositions of the subunits of ICSH, TSH and FSH from several species and those of HCG and PMSG are known (Tables 4-6). In the case of hormones where the complete primary structure has been determined, the theoretical values are included. It is apparent from Table 4 that the amino acid compositions of all the ICSH α's are completely different from the respective β-subunits; particularly noteworthy are the reciprocal relationship in the content of Lys, Arg, Pro, Ile, Leu, Tyr and Phe in the two subunits. The data in Table 4 also show that the amino acid composition of HCG α is almost identical to that of human ICSH α. The number of amino acid residues in the β-subunit is slightly larger than the α-subunit.

The differences in the amino acid compositions of the subunits of TSH (Table 5) and FSH (Table 6) do not reveal drastic changes, except for a few residues. Table 6 also shows the amino acid composition of PMSG.

TABLE 4 — AMINO ACID COMPOSITION OF ICSH SUBUNITS*

Amino acid	Ovine		Porcine		Equine		Murine		Human		HCG	
	α	β	α	β	α	β	α	β	α	β	α	β
Lysine	10	2	10	0	5	2	10	1	6	2	6	4
Histidine	3	3	3	1	2	1	4	1	3	3	3	1
Arginine	3	8	3	10	4	5	3	9	3	10	3	12
Aspartic acid	6	5	4	5	5	4	7	6	5	7	6	11
Threonine	9	7	9	6	7	6	8	8	8	7	8	10
Serine	6	8	6	10	5	7	7	9	8	7	8	12
Glutamic acid	8	6	7	6	7	6	7	6	9	7	9	9
Proline	7	20	5	20	6	13	7	20	6	16	7	24
Glycine	4	7	4	8	4	4	5	7	4	8	4	8
Alanine	7	8	8	11	5	9	8	9	4	5	5	8
Half-cystine	10	12	10	12	7	8	9	10	10	12	10	12
Valine	5	8	4	7	4	5	4	10	7	11	7	11
Methionine	4	3	4	1	1	1	3	2	3	2	3	1
Isoleucine	2	5	2	4	4	4	4	3	1	5	1	5
Leucine	2	12	3	13	4	6	4	11	4	8	4	14
Tyrosine	5	2	5	2	4	1	5	3	4	2	4	3
Phenylalanine	5	3	3	3	4	3	3	4	4	2	4	2
Tryptophan	0	0	0	0			0	0	0	1	0	0
Total	96	119	90	119					89	115	92	147

*The amino acid compositions of the α- and β- subunits of ovine, porcine, human ICSH and HCG are derived from primary structure Ovine and bovine ICSH subunits are identical. The values for equine and murine ICSH subunits are taken from refs. 31 and 32 respectively.

TABLE 5 — AMINO ACID COMPOSITION OF TSH SUBUNITS*

Amino acid	Human		Bovine		Porcine	
	α	β	α	β	α	β
Lysine	6	7	10	9	10	9
Histidine	3	3	3	3	4	4
Arginine	3	5	3	4	4	4–5
Aspartic acid	5	9	6	9	4–5	8–9
Threonine	8	11	9	11	9	9
Serine	8	5	6	5	6	5
Glutamic acid	9	7	8	7	9	9
Proline	6	7	7	7	6–7	8
Glycine	4	4	4	4	5	7
Alanine	4	6	7	6	8	6
Half-cystine	10	12	10	12	7	9
Valine	7	4	5	6	4–5	5
Methionine	3	2	4	5	4	3–4
Isoleucine	1	9	2	6	2	5
Leucine	4	6	2	4	4	5
Tyrosine	4	11	5	11	5	10
Phenylalanine	4	4	5	4	4	4
Total	89	112	96	113		

*The amino acid compositions of human and bovine TSH subunits are derived from primary structure. For porcine TSH, the data of Closset and Hennen[40] have been recalculated assuming the same number of total residues as in bovine TSH subunits.

TABLE 6 — AMINO ACID COMPOSITION OF FSH SUBUNITS AND PMSG*

Amino acid	Human		Ovine		Equine		PMSG	
	α	β	α	β	α	β	α	β
Lysine	6	7	8·8	5·3	10·8	7·8	6	3
Histidine	3	3	3·0	2·8	4·0	3·5	3	1–2
Arginine	3	5	2·9	4·7	5·5	3·4	5	6
Aspartic acid	6	10	5·5	9·8	8·6	12·4	7	5
Threonine	8	14	8·2	11·0	11·5	14·2	7	9
Serine	8	7	5·3	7·3	5·7	9·0	5	13
Glutamic acid	9	11	7·6	8·9	11·9	9·6	11	9
Proline	7	5	6·5	5·3	8·9	7·4	8	18
Glycine	4	6	3·5	5·2	6·1	8·9	7	8
Alanine	5	6	7·1	6·0	5·9	8·0	6	12
Half-cystine	10	12	8·4	10·4	11·1	10·9	8	7
Valine	7	6	5·0	6·7	7·0	8·2	4	6
Methionine	3	1	3·7	0	1·4	1·1	2	2–3
Isoleucine	1	6	2·2	5·7	6·7	5·6	4	6
Leucine	4	5	2·3	5·0	6·2	6·5	5–6	9
Tyrosine	4	7	4·6	6·5	5·8	7·8	4	2
Phenylalanine	4	3	3·8	3·0	7·3	3·2	5	4
Tryptophan	0	1	1·6	2·6				
Total	92	115						

*Composition of human FSH is derived from primary structure. Values for ovine FSH subunits are from ref. 34, equine from ref. 36, recalculated - PMSG from ref. 43. The reported values for PMSG have been recalculated on the assumption that the α-and β-subunits contain 96 and 119 residues respectively.

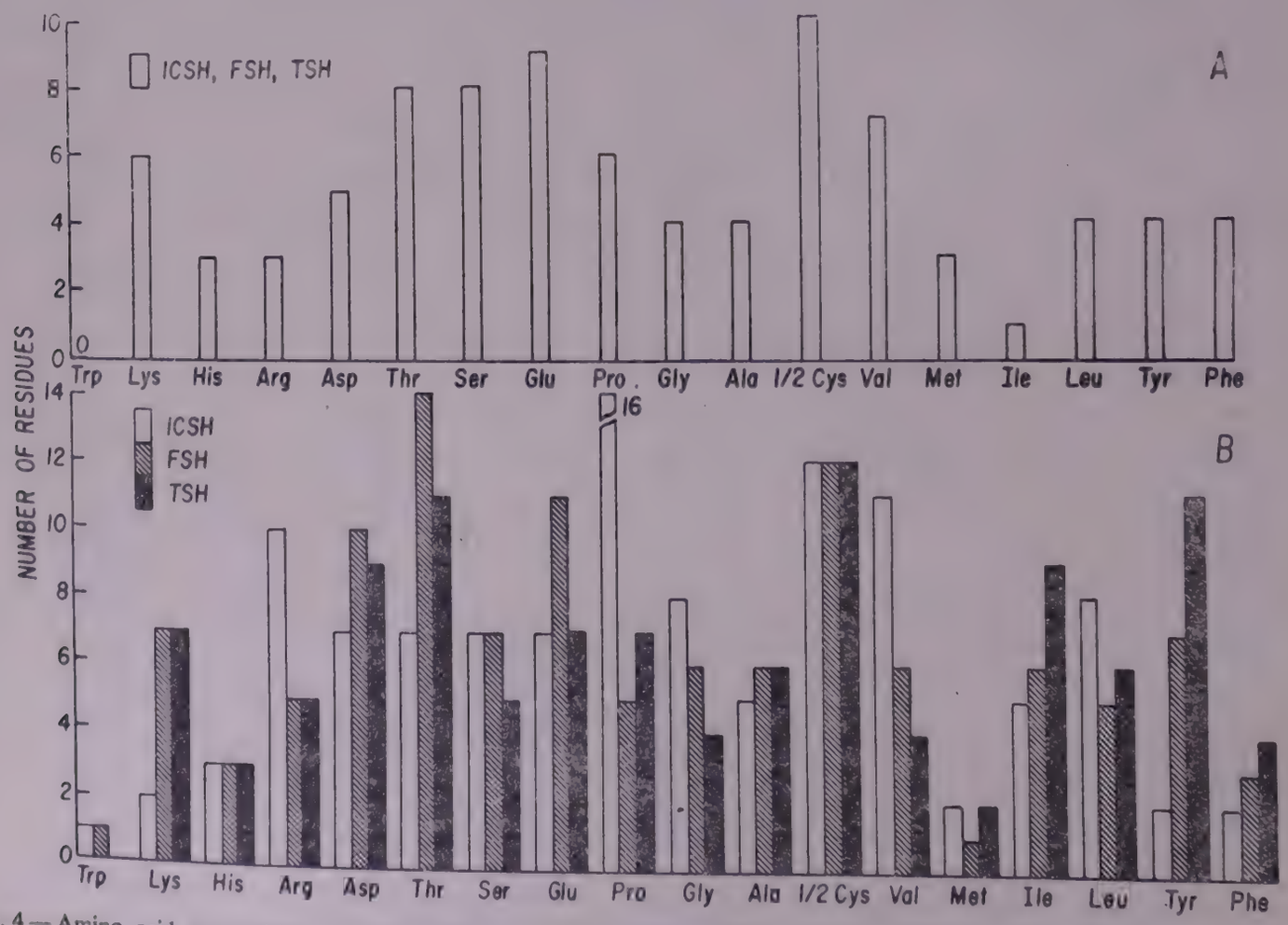

Fig. 4 — Amino acid composition of the subunits of human pituitary ICSH, FSH and TSH [A: The composition of the α-subunits in all the three hormones is identical[39,66,76]. The α-subunit of FSH in ref. 75 has an additional residue of Ala, Pro and Asp. B: Composition of the β-subnits[67,77,71]]

Examination of the amino acid composition data indicates the following points. In human species, where all the three pituitary hormones ICSH, TSH and FSH and placental HCG have been sequenced, the composition of the α-subunit is virtually identical in all the hormones. The β-subunits, however, are different (Fig. 4). The same conclusion can be extended to bovine TSH and ICSH as well as porcine TSH and ICSH. Tryptophan is absent in human TSH and β- subunits of the three hormones have the same number of half-cystine residues. The h-ICSH β has an unusually high proportion of hydrophobic amino acid residues, proline, in particular.

(b) *Carbohydrate composition* — Although the data on the carbohydrate composition of subunits of most of the glycoprotein hormones except that of human FSH are available, these are to be treated as tentative until the complete sequence of monosaccharides in the two subunits becomes known.

Carbohydrate compositions of the two subunits of human ICSH, TSH and HCG are given in Table 7. Data for other species can be found in literature[2,3]. In the three pituitary hormones, the α-subunit has clearly much higher percentage of carbohydrate than the β-subunit. In HCG, which is of placental origin, the reverse is true.

(c) *Primary structure of the subunits* — The most fascinating aspect of the chemistry of the glycoproteins in recent years has been the elucidation of their complete amino acid sequence which has provided a chemical basis for their similarities. The amino acid sequences of ovine ICSH and bovine TSH were simultaneously determined in three different laboratories. The structure of bovine pituitary TSH was determined by Liao and Pierce[63] and that of ovine ICSH α and β by Sairam *et al.*[64,14] and Liu *et al.*[65,12]. Since then the amino acid sequences of subunits of human ICSH[66–68], bovine ICSH[13,69], porcine ICSH[13,70], human TSH[39,71], HCG[72–74], have been determined. The only data available on FSH are those of human[75–77].

Sequence determination in most cases was done by the conventional methods utilizing manual dansyl-Edman degradation technique. In some cases, such as HCG and ovine ICSH, the semiautomatic sequenator was utilized. But, in general, the sequenator has not been that helpful in solving these difficult structures. For the sake of brevity, our own studies on human ICSH subunits are briefly discussed here as an example. A particular difficulty of all the investigators working with human pituitary hormones is the scarcity of material, especially at the stage of subunits. At the beginning of our investigation on the amino acid sequence of h-ICSH α[66], we relied on the information already available for the whole molecule (without subunit separation) of the ovine hormone.

The cyanogen bromide fragments, tryptic peptides, were sequenced and aligned on the basis of homology with ovine ICSH-α[64]. These data were later confirmed by the isolation and complete sequence analysis of the tryptic peptides obtained from the isolated α-subunit. The structure of h-ICSH-β was determined by similar degradative procedures on the isolated subunit preparations. The two-dimensional paper chromatography-electrophoretic technique proved very useful in the isolation of all the tryptic and chymotryptic peptides required for complete sequence analysis. The complete amino acid sequence, including the location of amides of human ICSH α- and β-subunits, as formulated by us, can be seen in Fig. 5.

The α-subunit has 89 amino acid residues with valine at the NH_2-terminus and serine at the COOH-terminus. The β-subunit is larger with 115 residues with a free serine at the NH_2-terminus. There is a slight degree of heterogeneity at the NH_2-terminus of the α-subunit and considerable heterogeneity at the terminus of the β-subunit. The two oligosaccharide moieties in the α-subunit are linked to asparagine residues at positions 49 and 75. The single carbohydrate moiety in the β-subunit is similarly covalently linked to an asparagine residue at position 30 along the sequence. The single Trp residue in h-ICSH-β is found in position 8.

(d) *Structure of the carbohydrate units* — Investigations on the pituitary ICSH and TSH, whose primary structures have been investigated, have revealed that they contain three oligosaccharide moieties —

TABLE 7 — CARBOHYDRATE COMPOSITION* OF HUMAN ICSH, TSH AND HCG

Sugar	Human ICSH			Human TSH			HCG		
	Native	α	β	Native	α	β	Native	α	β
Fucose	1·64	0·5	1·2	1·4	0·5	1·1	2	0·06	1·66
Mannose	10·4	6·6	3·4	9·2	7·2	3·0	12–14	8·94	6·74
Galactose	5·0	2·8	1·9	2·0	2·0	0·7	12–14	3·94	7·88
N-Acetyl glucosamine	10·8	8·0	4·5	8·1	7·3	2·7	16–18	7·37	8·97
N-Acetyl galactosamine	3·5	2·5	1·1	3·8	3·5	1·4	3	0·02	2·37
Sialic acid	3·05	2·2	1·36	1·9	1·6	0	10–11	4·84	6·93

*Residues per molecule. No reliable data are available on h-FSH subunits. For HCG, the data of Bahl[4] have been recalculated.

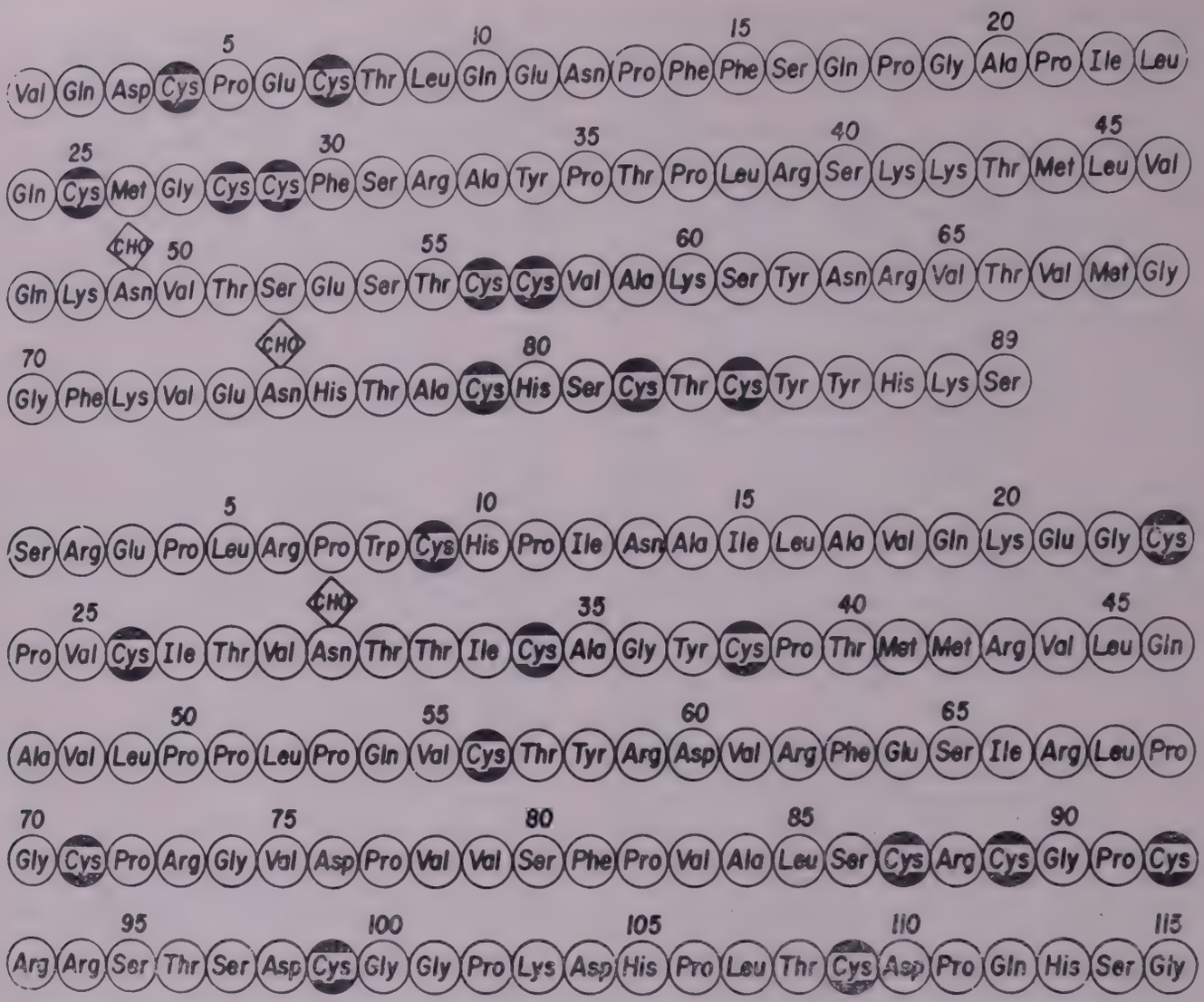
Val Gln Asp Cys Pro Glu Cys Thr Leu Gln Glu Asn Pro Phe Phe Ser Gln Pro Gly Ala Pro Ile Leu
Gln Cys Met Gly Cys Cys Phe Ser Arg Ala Tyr Pro Thr Pro Leu Arg Ser Lys Lys Thr Met Leu Val
CHO
Gln Lys Asn Val Thr Ser Glu Ser Thr Cys Cys Val Ala Lys Ser Tyr Asn Arg Val Thr Val Met Gly
CHO
Gly Phe Lys Val Glu Asn His Thr Ala Cys His Ser Cys Thr Cys Tyr Tyr His Lys Ser
Ser Arg Glu Pro Leu Arg Pro Trp Cys His Pro Ile Asn Ala Ile Leu Ala Val Gln Lys Glu Gly Cys
CHO
Pro Val Cys Ile Thr Val Asn Thr Thr Ile Cys Ala Gly Tyr Cys Pro Thr Met Met Arg Val Leu Gln
Ala Val Leu Pro Pro Leu Pro Gln Val Cys Thr Tyr Arg Asp Val Arg Phe Glu Ser Ile Arg Leu Pro
Gly Cys Pro Arg Gly Val Asp Pro Val Val Ser Phe Pro Val Ala Leu Ser Cys Arg Cys Gly Pro Cys
Arg Arg Ser Thr Ser Asp Cys Gly Gly Pro Lys Asp His Pro Leu Thr Cys Asp Pro Gln His Ser Gly

Fig. 5 — Amino acid sequence of human ICSH α- and β-subunits (Upper, α-subunit; lower, β-subunit)

two in the α- and one in the β-subunit. On the other hand, the preliminary report on human FSH indicates the presence of four carbohydrate units[76,77]. This observation, however, needs to be confirmed. Apparently, two units are present in each of the two subunits. The placental gonadotropin HCG contains 7-8 oligosaccharide side chains, two being present in the α-subunit[72,74] and 5-6 in the β-subunit[73,74]. Two oligosaccharide chains in the β-subunit are of the N-glycosidic linkage, being linked to asparagine residues, while the rest are all of the O-glycosidic type[4]. The latter are linked to the serine residues near the COOH-terminus[73,74].

Very little progress has been made in the determination of the carbohydrate structure in the subunits of glycoprotein hormones. Whatever little information is available is restricted to HCG. Bahl[4], utilizing specific glycosidases to degrade the oligosaccharide chain from the non-reducing terminal sugar residue and identifying the released sugar by the gas chromatographic or colorimetric methods, has proposed tentative structures of the carbohydrate units in HCG α and HCG β (Fig. 6). Type I structure has been assigned to that present in the α- and type II to that in the β-subunit. The three other carbohydrate units in the β-subunit consist of short oligosaccharide chains made

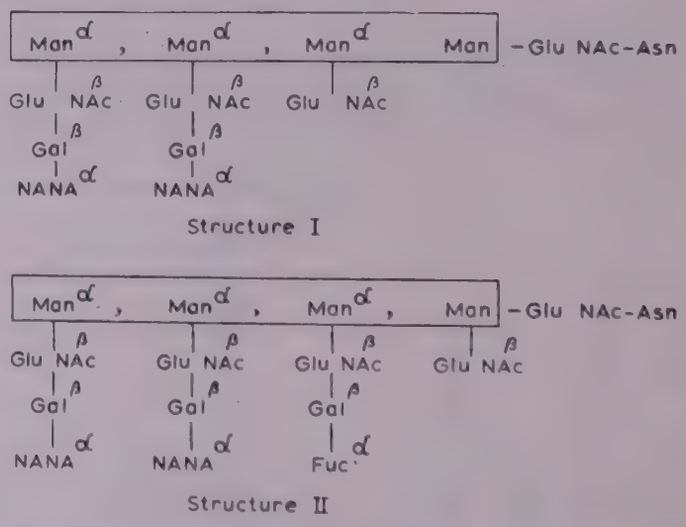
Man α , Man α , Man α Man
-Glu NAc-Asn
Glu β NAc Glu β NAc Glu β NAc
Gal β Gal β
NANA α NANA α
Structure I
Man α , Man α , Man α , Man
-Glu NAc-Asn
Glu β NAc Glu β NAc Glu β NAc Glu β NAc
Gal β Gal β Gal β
NANA α NANA α Fuc α
Structure II

Fig. 6 — Tentative structures of the carbohydrate units in HCG α and HCG β (Structure I, sequence of monosaccharides in the carbohydrate units of HCG α; Structure II, sequence of monosaccharides in the carbohydrate units of HCG β. Taken from ref. 4]

up of three residues each and linked to the polypeptide backbone through the N-acetylgalactosaminyl serine linkage. The invariant sequence –pro-ser (CHO)

found around the carbohydrate-linked serine residue in HCG β has been speculated as the recognition site for the N-acetylgalactosaminyl transferase to attach the oligosaccharide moiety to the polypeptide chain. Extensive studies into the oligosaccharide moieties of all the glycoprotein hormones are needed.

(e) *Structural similarities* — Before the advent of the modern concept of subunit structure of the gonadotropins and TSH, the only similarity and classification that enabled them to be grouped together into a single family was the fact that they all contained carbohydrate as the prosthetic group. Nearly 50 years after their discovery, the chemical basis of their relationship among these hormones has now been clearly established. In this section the comparison of the amino acid sequences of the different hormones is included.

The knowledge of the amino acid sequences of ICSH, TSH and HCG has enabled detailed comparisons of the structures of the subunits not only within the species but also between different species. A comparison of the amino acid sequences of the α-subunits of ICSH from four species shows that the sequence of the α-subunits of ovine and bovine ICSH, which are 96 amino acid residues long, are identical (Fig. 7). In addition to the chain being shorter by six residues at the amino terminus, there are only three differences between porcine ICSH-α and ovine ICSH-α. The human ICSH-α subunit, however, differs to a greater degree. Between human and ovine, there are 21 differences. The human ICSH-α has only 89 amino acid residues. The overall homology among the various α-subunits is nearly 70%. It is particularly important to note that all the 10 half-cystine residues occupy identical positions. The amino acid sequence of HCG-α is identical to that of human pituitary ICSH-α, except that the former has an additional tripeptide Ala-pro-Asp- at the amino terminus. Some human ICSH-α chains may also have this additional tripeptide at the—NH_2 terminus. The two oligosaccharide moieties of all the α-subunits are linked to asparagine residues occupying identical positions. The invariant sequence asn (CHO)–x–Thr around this asparagine has been postulated as the recognition site for the enzyme which attaches the N-acetylglucosamine to the amide group of asparagine in an N-glycosidic linkage[78]. The fact that some α's are shorter at the amino terminus, is suggestive of the fact that these may not be too important for activity. It should be noted that, in this subunit, heterogeneity, where observed, has always been confined to the amino terminal portion only. A possible allelic polymorphism has been observed in bovine ICSHα.

Within a species, the amino acid sequence of α-subunits of ICSH, TSH and FSH is identical. This has been demonstrated in the human. The sequences of the α-subunits of all the three hormones and HCG are nearly the same. In another species, the bovine, the ICSH-α and TSH-α have been shown to be basically identical. According to current concepts, all the information necessary for the formation of the –S–S– bridges and the folding of the peptide chain (tertiary

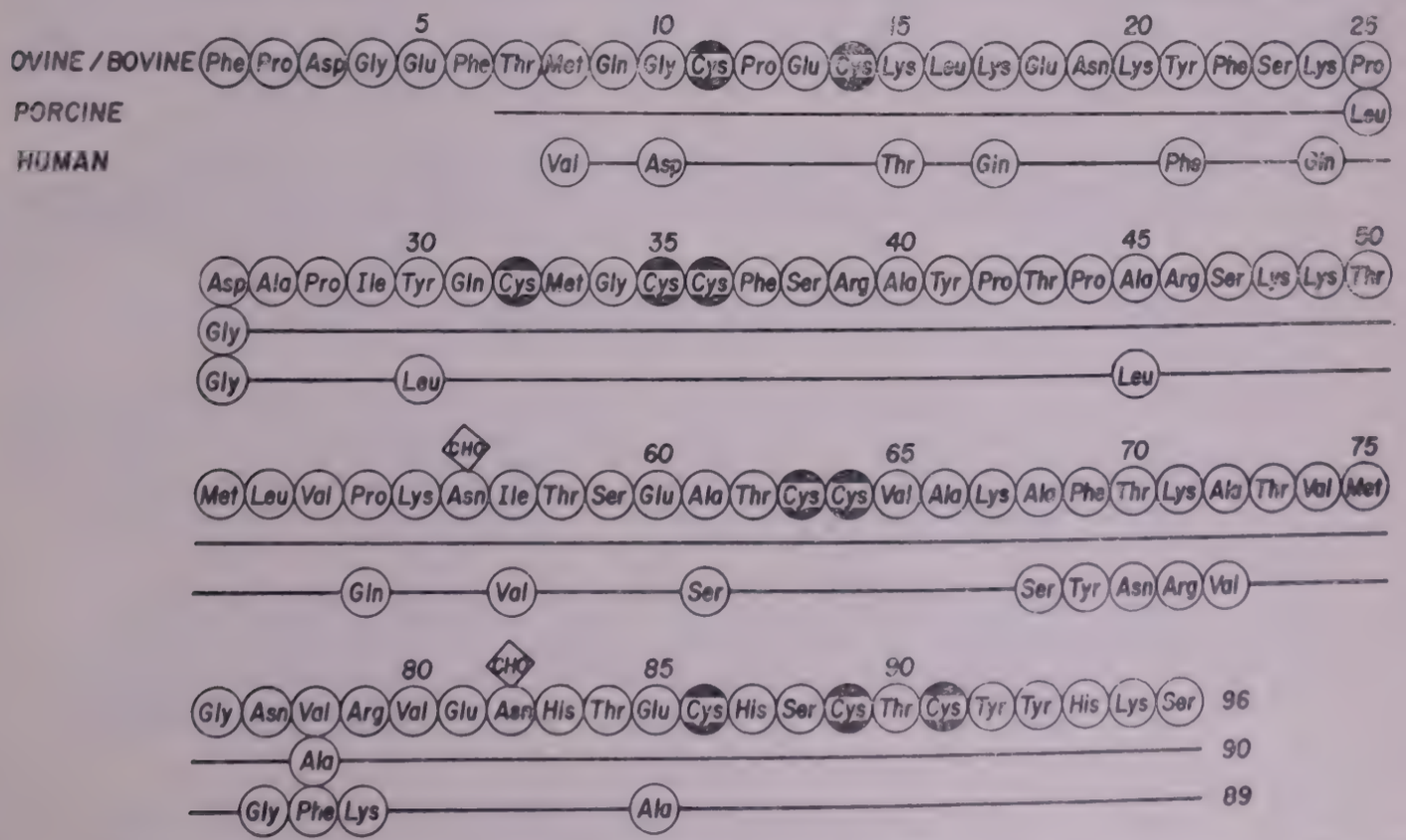

Fig. 7 — Comparison of amino acid sequences of the α-subunits of ICSH from different species [The sequences of ovine and bovine are identical. The positioning of residues 88 and 89 is as given in ref. 64 for ovine ICSH α. This is reversed in ref. 65 and other α-subunits compared. The HCG α is identical to human ICSH α, except for the presence of an additional tripeptide Ala-Pro-Asp at the $-NH_2$ terminus[72,74]. The solid line indicates identity. Positions of difference are shown. Data on positioning of amides are not in complete agreement]

structures) is contained in the linear amino acid sequence. We might, therefore, predict that the tertiary structures of the α-subunits of these hormones will be very similar if not completely identical. It must be pointed out that there are significant differences in the carbohydrate composition of the different α-subunits. For example, the content in HCG-α is much higher than that of pituitary ICSH-α; the content in bovine ICSH-α is less than that of ovine ICSH-α. What influence these may have on the tertiary structure of the α-subunit is not known at present and must await further studies.

The amino acid sequences of the β-subunit of ICSH from different species and of HCG-β have shown structural conservation (Fig. 8). Human ICSH β is unique in that only this has a tryptophan residue located at position 8. Unlike the α-subunit, a single gap is necessary to get a perfect alignment of all the 12 half-cystine residues. It may also be noted that, unlike non-human ICSH, the human ICSH β-subunit has its single carbohydrate moiety linked to asparagine at position 30 instead of 13. In all, a total of 69 amino acid residue positions have been conserved. The resemblance of human ICSH β to HCG β is greater than its similarity to other non-primate β-subunits. These two polypeptide chains differ to the extent of 19% of all residue positions. The interrelationships in structures of the subunits of ICSH of different species and HCG are summarized in Table 8.

The structural conservation in the β-subunits of bovine and human TSH is even greater (Fig. 9). In this hormone, the two sequences can be aligned perfectly without introducing any gaps. In all, there are only 11 different residue positions and even among these 10 can be accounted for on the basis of a single base change in the triplet code.

In the case of human, we are in a position to compare the sequence of the hormone specific β-subunits of ICSH, TSH and FSH (Fig. 10), despite certain uncertainties in the report on the latter hormone. The introduction of several gaps along the sequence in the three chains brings about the similarities in their structures. The most important feature to be recognized is the perfect alignment of all the 12 half-cystine residues in all the three chains. This fact suggests that the pairing of the six disulphide bridges is identical in all the three subunits. The β-subunits of the three different hormones also show substantial differences in their amino acid sequence. The position of attachment of the carbohydrate unit is the same in all the three hormones. However, FSH β is reported to have an extra moiety linked to an asparagine at position 7. In all, there are 27 residues that are identical. The identity between ICSH-FSH is

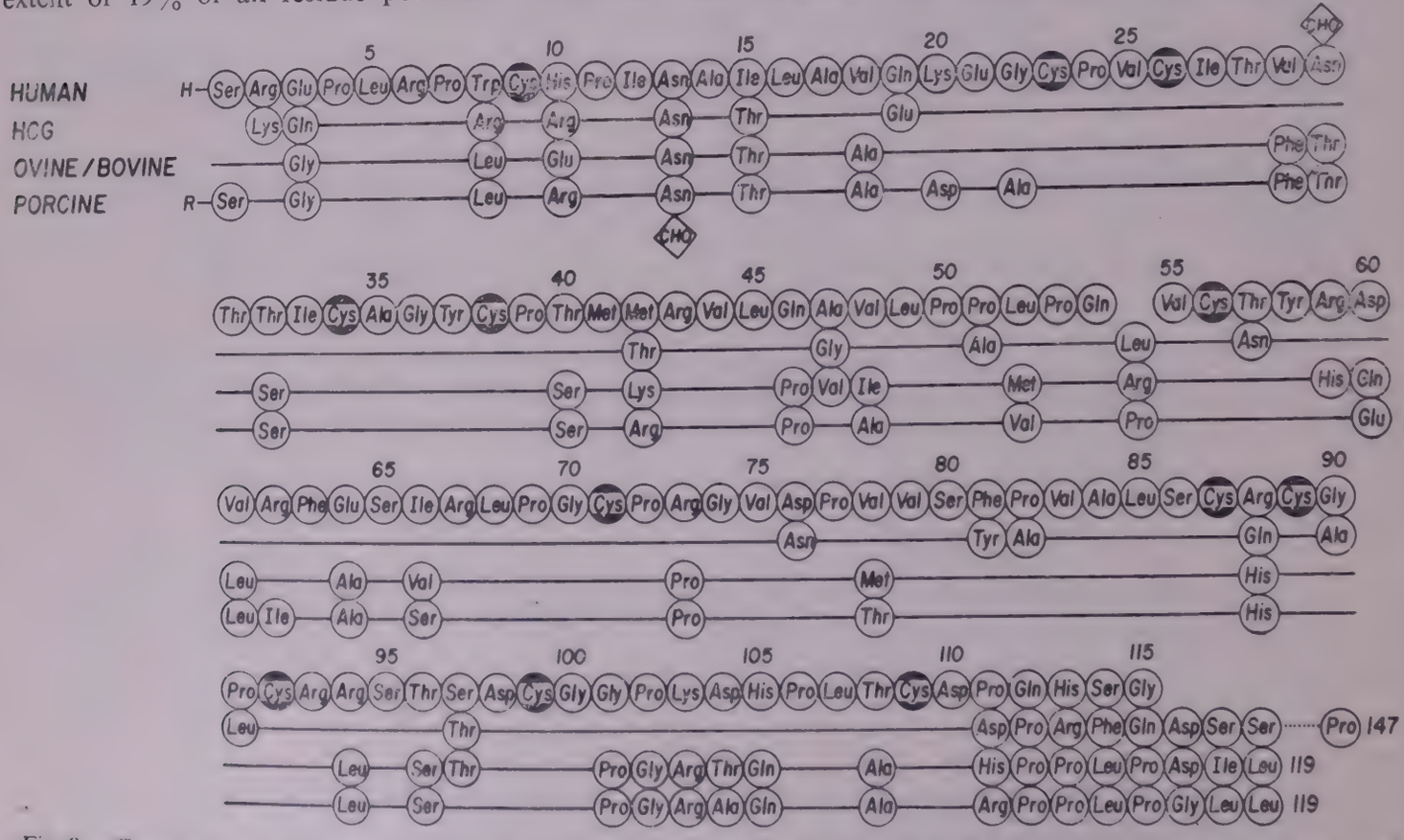

Fig. 8 — Comparison of amino acid sequences of ICSH β of different species and HCG β [Sequence given for ovine ICSH $\overline{\beta}$ is taken from refs. 12, 14 and 82, bovine and porcine[13] and human[67]. The human ICSH β as proposed in ref. 68 is somewhat different. The data on positioning of amides are not in complete agreement. The solid line indicates identity. In addition to the differences indicated, the HCG β has the additional following 31 residue peptide at the C-terminus:

CHO CHO CHO

Asp-Ser-Ser-Ser-Lys-Ala-Pro-Pro-Pro-Ser-Leu-Pro-Ser-Pro-Ser-Arg-Leu-Pro-Gly-Pro-Pro-Asx-Thr-Pro-Ile-Leu-Pro-Gln-Ser-Leu-Pro-OH. The sequence of HCG β selected here for comparison is that of Carlsen *et al.*[73] and is different in some respects from another report[74]]

TABLE 8 — STRUCTURAL HOMOLOGY AMONG ICSH OF DIFFERENT SPECIES

Species*	Ovine		Bovine		Porcine		Human		HCG	
	α	β	α	β	α	β	α	β	α	β
Ovine (96/119)			96 (100%)	119 (100%)	85 (88%)	106 (88%)	67 (70%)	77 (65%)	67 (70%)	75 (63%)
Bovine (96/119)	96 (100%)	119 (100%)			85 (88%)	106 (88%)	67 (70%)	77 (65%)	67 (70%)	75 (63%)
Porcine (90/119)	85 (88%)	106 (88%)	85 (88%)	106 (88%)			65 (72%)	80 (67%)	65 (70%)	74 (51%)
Human (89/115)	67 (70%)	77 (65%)	67 (70%)	77 (65%)	65 (72%)	80 (67%)			89 (97%)	96 (66%)
HCG (92/147)	67 (70%)	75 (63%)	67 (70%)	75 (63%)	65 (70%)	74 (51%)	89 (97%)	96 (66%)		

*Numbers in parentheses indicate the amino acid residues in α- and β-subunits respectively. In cases where amides have not been designated, identity has been assumed.

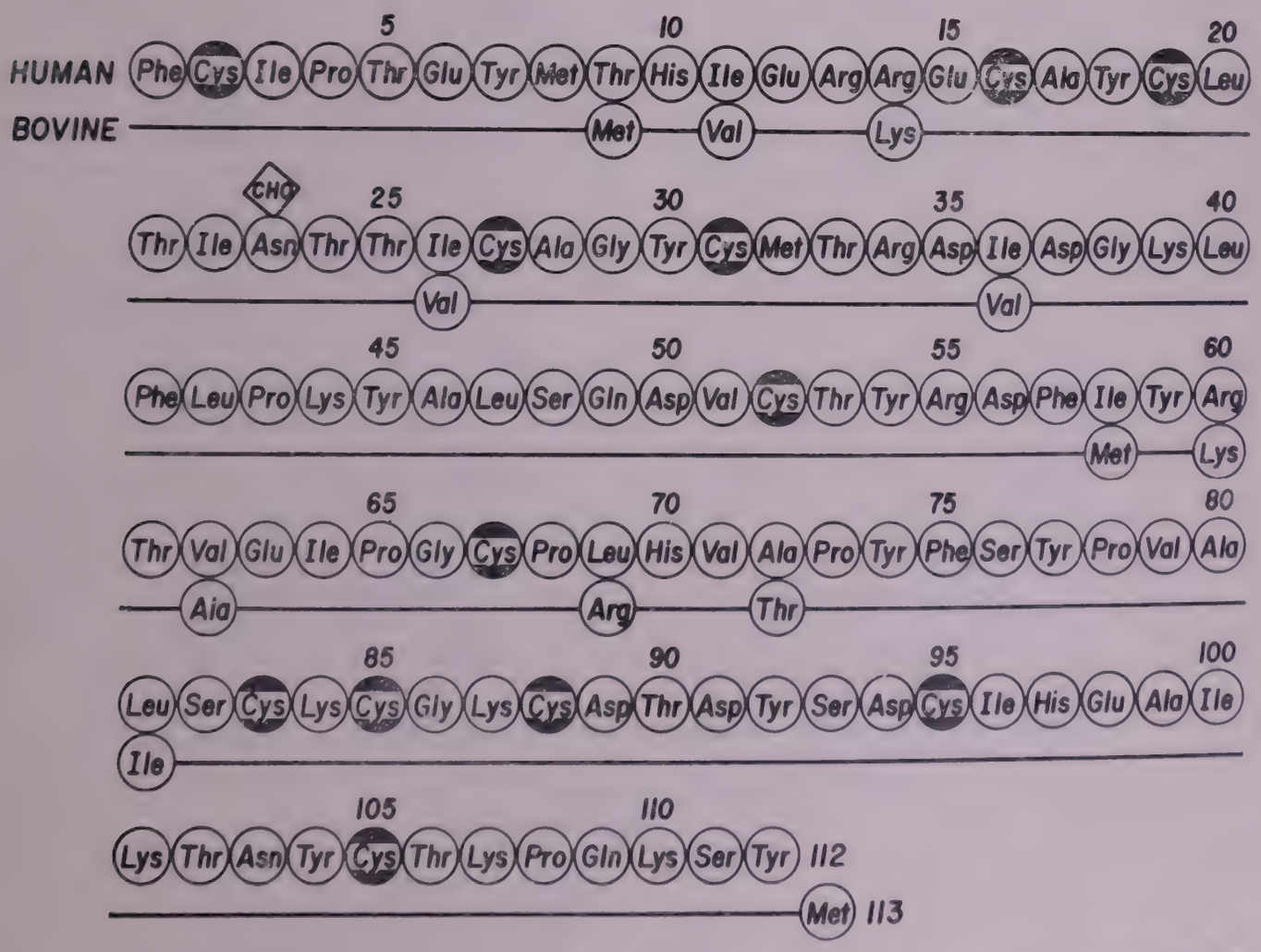
HUMAN
BOVINE
CHO
Phe Cys Ile Pro Thr Glu Tyr Met Thr His Ile Glu Arg Arg Glu Cys Ala Tyr Cys Leu
Met Val Lys
Thr Ile Asn Thr Thr Ile Cys Ala Gly Tyr Cys Met Thr Arg Asp Ile Asp Gly Lys Leu
Val Val
Phe Leu Pro Lys Tyr Ala Leu Ser Gln Asp Val Cys Thr Tyr Arg Asp Phe Ile Tyr Arg
Met Lys
Thr Val Glu Ile Pro Gly Cys Pro Leu His Val Ala Pro Tyr Phe Ser Tyr Pro Val Ala
Ala Arg Thr
Leu Ser Cys Lys Cys Gly Lys Cys Asp Thr Asp Tyr Ser Asp Cys Ile His Glu Ala Ile
Ile
Lys Thr Asn Tyr Cys Thr Lys Pro Gln Lys Ser Tyr 112
Met 113

Fig. 9 — Comparison of the structures of human TSH β^{71} and bovine TSH β^{63} [The solid line indicates identity. Differences are shown in full]

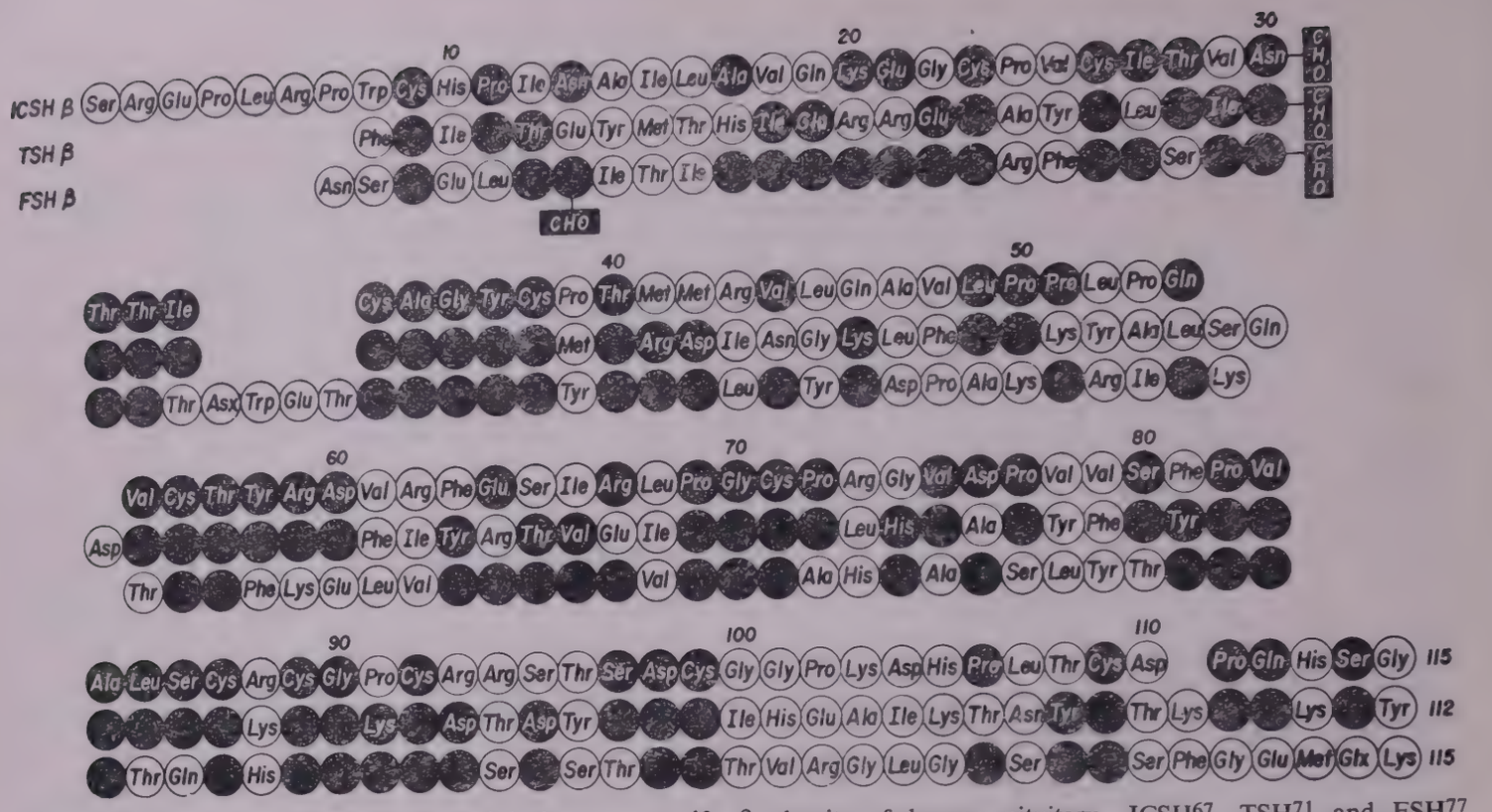

Fig. 10 — Comparison of the structures of the hormone specific β-subunits of human pituitary ICSH[67], TSH[71] and FSH[77] [The black circles indicate positions of identity among the β-subunits. There is uncertainty in several parts of the FSH β preliminary sequence as reported[77]]

38 (33%), ICSH-TSH 46 (40%) and TSH-FSH 44 (38%).

The comparison of bovine TSH β and bovine ICSH β also substantiates the fact that there is a certain degree of homology in the structures of the hormone specific subunits. Some homology is also seen between the structures of the α- and β-subunits of a given hormone (example ICSH or TSH). However, in this case, the introduction of fairly large gaps, though arbitrary, is required to detect maximum similarities. These are confined to short regions of the sequence; six half-cystine residues are in identical positions.

From the above comparisons of the structures of the subunits of these hormones not only within a species but also between different species, the following features can be readily recognized: (i) the sequences of the ovine and bovine ICSH are identical, (ii) the α-subunit has slightly fewer amino acid residues than the β-subunit, (iii) microheterogeneity, where present, appears to be confined to the amino terminal of the α-subunit and the carboxyl terminal of the β-subunit, (iv) there is a high degree of conservation in structure and many of the changes can be considered as acceptable replacements, (v) the hormone specific β-subunit of a hormone is more resistant to change than the α-subunit, (vi) the α-subunits of ICSH, FSH and TSH are identical in a given species, (vii) although the β-subunits of the three hormones are different, there is a certain degree of homology among them, (viii) the 10 half-cystine residues in the α-subunits occupy identical positions and so do the 12 half-cystines in the β-subunits, suggesting that the –S–S– bridges in the respective subunits must be identical, and (ix) the α-subunits, in general, possess two oligosaccharide moieties, whereas the β-subunits have only one. The placental gonadotropin β-subunits are an exception to this.

(f) *Disulphide bridges* — From the discussion in the previous sections, it is clear that the gonadotropins and TSH have a large number of disulphide bonds. There are a total of 11 of them (five in the α- and six in the β-subunit) as compared to two for pituitary growth hormone and three for prolactin. The disulphide bridges in a protein are part of the several forces that serve to stabilize the molecular architecture and maintain the molecule in its native conformation. As such, the information on the primary structure is incomplete without the assignment of these bonds in a protein.

Because of the presence of such a large number of disulphide bonds in these hormones, their determination has been an extremely difficult task. This is further complicated by the fact that in the α-subunits, four of the 10 half-cystine residues are located adjacent to one another. Different approaches have been used to solve this problem and unfortunately there is no agreement in the reports from different laboratories. We have used enzymic as well as partial acid hydrolytic degradations to isolate and identify the different -S-S- containing peptides. Fig. 11 shows the primary structure of the ovine ICSH α-subunit 79 with the 5 disulphide bridges formed by residues at positions 11-64, 14-86, 32-89, 35-63 and 36-91. This is in disagreement with the report of Cornell and Pierce[80], who have proposed the pairings 11, 14 with either 35, 36 or 36 and 35, 32-64, 63-91 and 86-88. Yet another group[81] has presented a tentative formulation for porcine ICSH α, which agrees with neither of the two above pairings. Such wide discrepancies only go to show

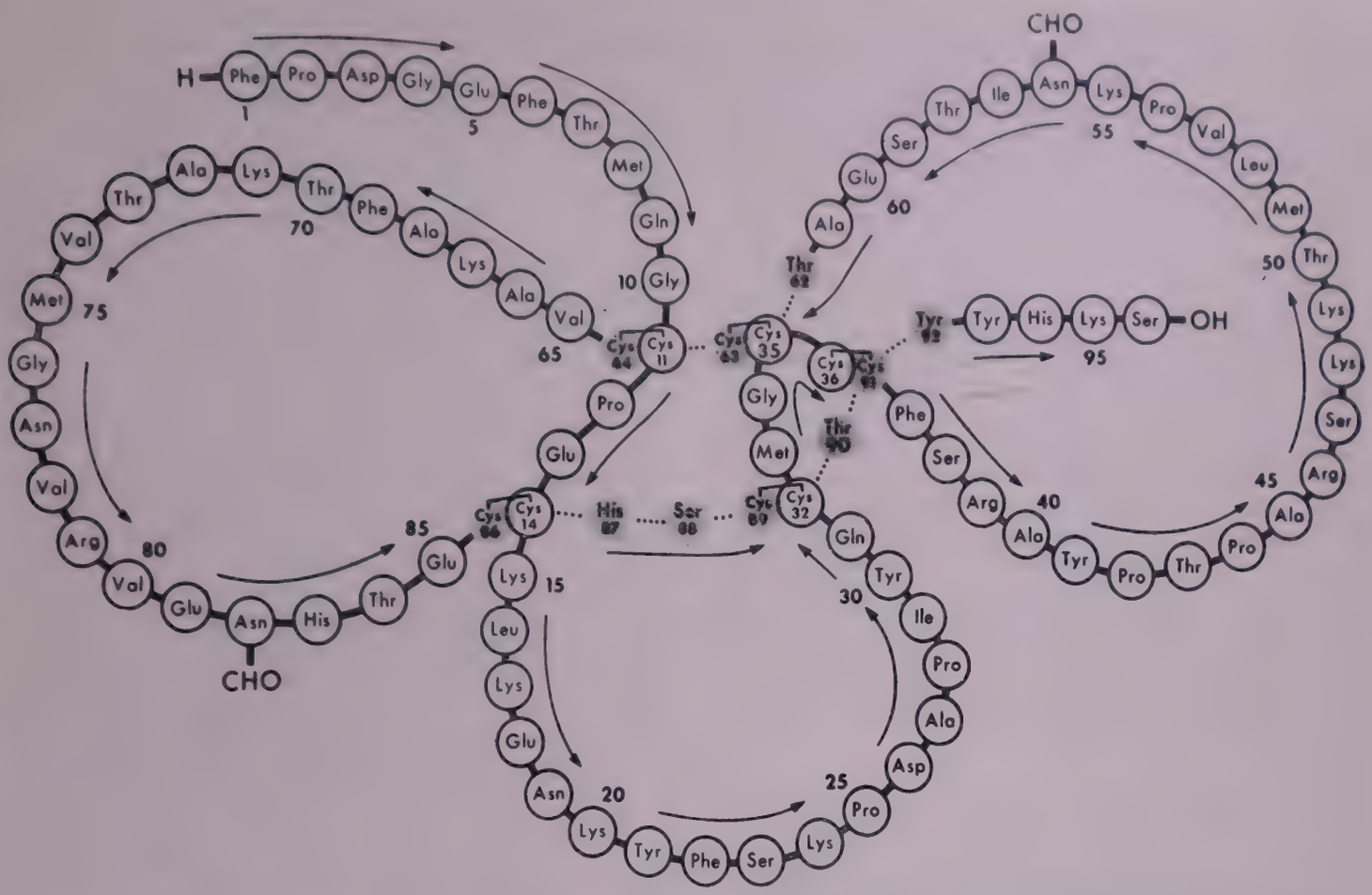

Fig. 11 — Primary structure of the ovine ICSH α-subunit as reported in ref. 79 [The five disulphide bridges are formed between residues 11-64, 14-86, 32-89, 35-63 and 36-91]

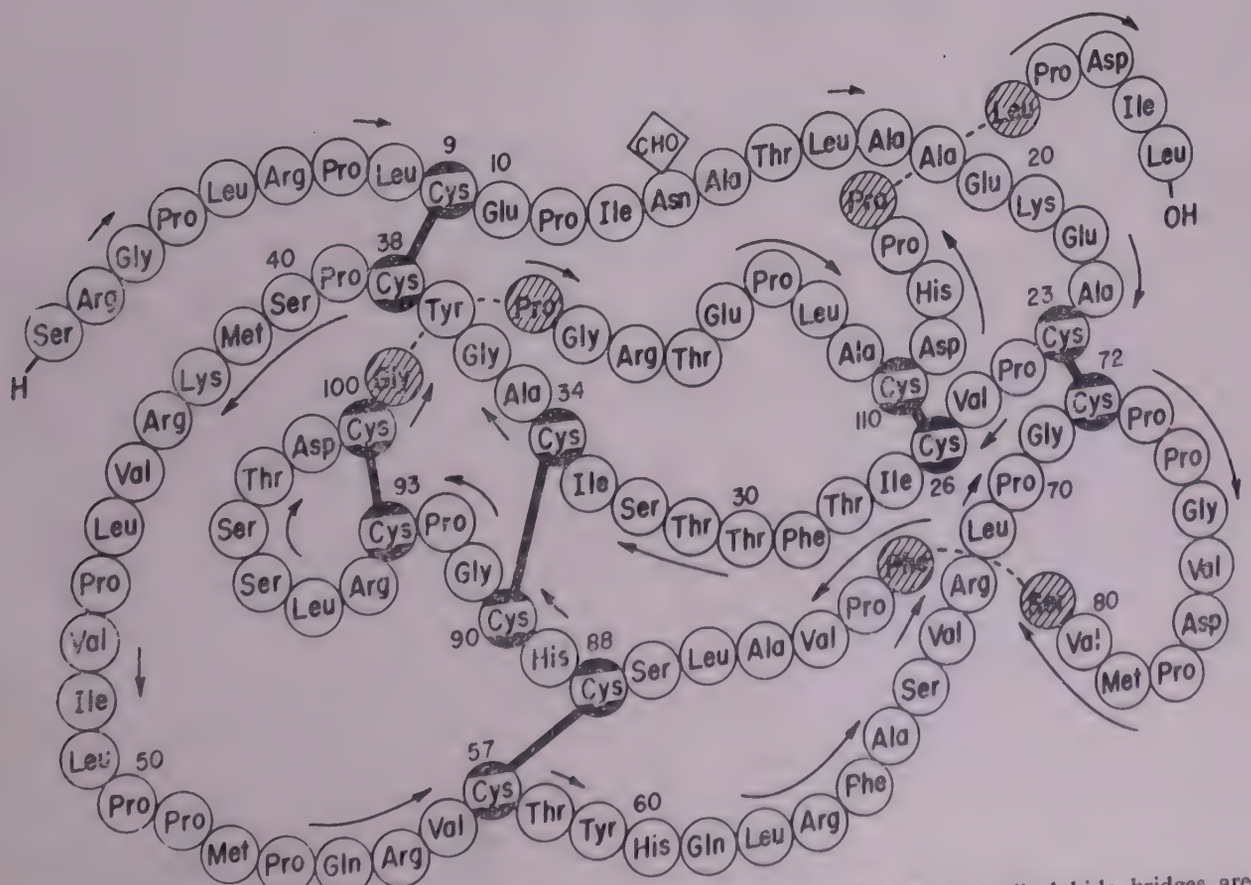

Fig. 12 — Primary structure of the ovine ICSH β subunit [Taken from ref. 82. The six disulphide bridges are formed between residues 9-38, 23-72, 26-110, 34-90, 57-88 and 93-100. The pairs 23-72 and 26-110 are in agreement with that of Ward *et al.*[83]. The link 93-100 has also been proposed by Reeve *et al.*[84]]

that enormous difficulties are encountered. Perhaps better techniques in future will provide a clarification.

The six -S-S- bridges in the primary structure of ovine ICSH β link Cys residues 9-38, 23-72, 26-110, 34-90, 57-88 and 93-100[82] (Fig. 12). Two of these are in agreement with the tentative proposals of Ward *et al.*[83]. A recent report[84] using the partial reduction approach on the bovine ICSH β substantiates our proposal for one of the -S-S- bridges between residues 93-100. Thus, there appears to be some agreement in the proposal from different laboratories on the ICSH β. As discussed earlier, the number and positions of the half-cystine residues in the α-subunits of the different hormones and so also of the β-subunits are the same. Based on the formulations of the -S-S- bridges in the ovine ICSH α and β, one may predict that the same will hold true for the subunits of other hormones. The pairings of six bridges in the β-subunits of TSH, FSH and ICSH will probably be identical. First indication that this is indeed true is provided by the recent observations of Reeve *et al.*[84] that homologous Cys residues (88-95 in bovine TSH β and 93-100 in bovine ICSH β) participate in -S-S- bond formation. It swill be extremely interesting to see if the prediction will hold true for the other 5 disulphide bridges in the molecule as well.

VII. Evolutionary Aspects

The evolutionary aspects of a particular class of proteins have often been assessed by a comparison of their properties and detailed amino acid sequences derived from various species. The pituitary gland provides one of the best examples of evolution in which related molecules have been put to different biological functions, viz. oxytocinvasopressin, ACTH-MSH, GH-Prl-HCS and the glycoproteins. A recent review has considered these aspects of hormones in detail[85]. In the case of glycoprotein hormones, detailed information on the properties and sequence is restricted to only a few mammalian species and thus any consideration of their evolutionary patterns must remain speculative.

It is now firmly established that the pituitary and placental gonadotropins and TSH have a subunit nature which is closely related in structure. Based on the structural homologies demonstrated in the few species, one might speculate that the subunits and the five different hormones may have evolved from a common ancentral precursor. Further, this precursor might have been a single polypeptide chain. This must, of course, await work on similar hormones in non-mammalian species. Preliminary information available on reptilian (turtle)[86] and amphibian (frog)[87] ICSH has already revealed the presence of a subunit structure. From an evolutionary point of view, it will be extremely interesting to see whether some other member of the lower vertebrate class may indeed have a single polypeptide chain gonadotropin or TSH. This might either be a simple protein or a glycoprotein.

One can find analogies in the chemical make up of the different hemoglobins and the glycoprotein hormones. Both have a quaternary structure and the α-chain in both classes seems to have been preserved to a great extent.

VIII. Immunochemical Considerations

The glycoproteins are, in general, excellent antigens, i.e. antibodies can be raised against them fairly easily. A possible exception to this is perhaps some species of FSH. A problem that has beenencountered frequently in the development of immunoassay techniques has been that of absolute specificity of the antibody employed. This, of course, is dependent upon the purity of the antigen and the host animal used for immunization; different individuals might elicit varied population of antibodies. An adequate explanation of the cross-reactivities observed between the so-called highly purified glycoprotein hormones was not forthcoming until the discovery of their subunit structure and the close similarities. Many early observations have indicated that the problem of specificity is more complicated than mere contamination by other hormones. For instance, antisera prepared against human pituitary TSH cross-reacted well with HCG (a hormone which is of placental origin). It is unlikely then that a pituitary hormone could be contaminated with one from the placenta. This was suggestive of the fact that these two molecules, though being different hormones, must share similar antigenic determinants. As detailed in the earlier sections, the similarities in the structures of this family of hormones not only within a species but also between species have been clearly established. On this basis, it is now thought that the common α-subunit present in all the three hormones accounts to a large degree for the immunological cross-reactivities.

The availability of highly purified α- and β-subunits of the different hormones has led to the preparation of antibodies against them and to a detailed study of the cross-reactivities in the entire family of molecules.

These studies have demonstrated that the β-subunit, in addition to conferring biological specificity to the α- and β-complex (hormone), also confers immunological specificity. The recent revelations on the quaternary structure of the pituitary and placental glycoprotein hormones have, in addition to formulating a basis for understanding the cross-reactivities, also provided the necessary tools for the development of highly specific radioimmunoassays. Thus, for instance, HCG β has been used as an antigen to develop a radio-immunoassay in which two very closely related hormones (both in structure and function), placental HCG and human pituitary ICSH, can be discriminated[88] and this has thus provided a new sensitive and specific technique for the detection of early pregnancy in the human. A comparison of the amino acid sequence of HCG β and H-ICSH β (Fig. 8) reveals that the former has an additional 30-32 residue peptide fragment at the C-terminus. This difference in structure along with the possible conformational differences imposed by the presence of the extra carbohydrate moieties can possibly account for the generation of additional antigenic determinants in HCG β.

A sampling of the various immunological cross-reactivities among the glycoprotein hormones and subunits is shown in Table 9[89]. On this basis, it has been suggested that the cross-reactivities between hormones are determined by the common antigenic determinants found in the α-subunits. However, the

TABLE 9 — IMMUNOLOGICAL CROSS-REACTIVITIES* AMONG GLYCOPROTEIN HORMONES AND SUBUNITS

Preparation	Antisera			
	Anti-ICSHα_h	Anti-ICSH β_h	Anti-HCG α	Anti-HCGβ
h ICSH	+	+	+	I
ICSHα_h	+	+C	+	+C
ICSHβ_h	+C	+	+C	I
h FSH	+	+C	+	I
FSHα_h	+	—	+	—
FSH-β_h	—	I	+C	I
HCG	+	I	+	I
HCG-α	+	—	+	+C
HCG-β	I	+	+C	+
h TSH	+	I	+	I
TSH-α_b	NI	NI	—	—
TSH-β_b	NI	NI	—	—
ICSH-α_b	NI	—	—	—
ICSH-β_b	—	+	—	—
ICSH-β_r	—	+	—	—
ICSH-α_r	NI	—	—	—
ICSH-α_o	NI	—	—	—
ICSH-β_o	—	+	—	—

h, human; b, bovine; O, Ovine; r, rat;
* Adapted from ref. 89.
\+ denotes complete inhibition with parallel dose response curves
I denotes incomplete inhibition with non-parallel dose response curves.
NI denotes no inhibition
— denotes not tested
+C denotes complete inhibition probably reflecting cross-contamination with either intact ICSH complementary subunit or its native hormone.

cross-reactivity among different species of a given hormone, for instance ICSH, resides in its hormone specific β-subunit.

IX. Biophysical Studies

Investigations on the conformational aspects of the glycoprotein hormones are limited to a few hormones. Studies in this direction have been done mainly with ovine and human ICSH, bovine TSH and HCG and their subunits and have shown that the content of proline and glycine and the number of disulphide bonds are high at least in ICSH and HCG, thereby minimising the possibility of the presence of any significant degree of ordered secondary structure. None of these hormones has any α-helical conformation, as shown by CD studies[90,91]. Using ovine ICSH and its subunits, it has been shown that significant conformational changes do occur upon dissociation of the hormone and that these changes are completely reversed upon reassociation of the two subunits under proper conditions[91]. Moreover, the side chain CD absorption spectra of the native and reassociated ICSH have been interpreted as indicating that one or more (two) tyrosines are present in a hydrophobic environment. This has been further substantiated by nitration of the tyrosine reisudes in ovine ICSH; two tyrosines, one in each subunit, were found to be inaccessible to the reagent[92]. Like ovine ICSH, the human hormone also does not have any appreciable amount of ordered secondary structure[93] and the difference spectra of native hormone and subunits have been taken to indicate likely changes in conformation upon dissociation/reassociation with the aromatic amino acid residues being implicated[94]. Neither the native nor the asialo HCG has any α-helical content[95]. Minor changes in conformation of the native and asialo hormone are suggested by the observation that the tyrosine residues in the latter are more easily accessible. The native HCG and its subunits rearrange to an ordered structure, in the presence of high concentrations of hexafluoropropanol, containing mainly α-helix components[96].

The CD spectra of bovine ICSH and TSH are very similar[97]. The larger maximum at 230-240 nm of TSH has been attributed to the higher tyrosine content in its β-subunit. The CD spectrum of the native hormone is not equivalent to the algebraic sum of the spectra of the individual subunits. As in the case of ovine ICSH, some conformational changes are indicated after recombination of the subunits.

Of all the glycoprotein hormones so far investigated, only FSH has an appreciable amount of secondary structure. The α-helix content of native ovine FSH has been estimated to be about 30%[98]. This ordered secondary structure is disrupted by denaturing conditions, such as 8 *M* urea or strong alkali. While the loss of α-helix caused by urea treatment is completely reversible, the changes induced by alkali are irreversible.

CD studies show that native human FSH has approximately 16% α-helix content and this is completely lost following urea treatment[99]. The isolated

α- and β-subunits show little α-helicity. Thus, as in the case of other hormones, the dissociation of the native hormone results in a drastic change in conformation. The recombined human FSH does not have a conformation identical to that of the native hormone. Strangely, the recombined molecule has an increased α-helical content of 40%. These observations strongly suggest that the two isolated subunits can possibly combine in ways that can result in conformations different from that of the native hormone. However, only those molecules which have a conformation close to or identical with that of the native hormone will be capable of exerting biological activity. On the other hand, if the subunits are altered or structurally damaged during isolation, the $\alpha+\beta$ complex could give rise to conformations different from that of the native. More detailed studies are needed from FSH of other species.

The kinetics of dissociation and reassociation of ICSH and HCG have been scrutinized carefully by biophysical techniques. Mainly two approaches have been adopted in these investigations. The first one takes advantage of the enhancement of fluorescence of a probe such as 8-anilino-1-naphthalene sulphonate (ANS) upon binding to either human ICSH or HCG. The fact that ANS does not bind to either the isolated α- or β-subunits provides a convenient method to follow dissociation and reassociation[100,101]. In other recent studies, advantage was taken of the fact that there is a significant change in CD spectra of ovine ICSH upon dissociation and reassociation of the subunits[91,102]. The presence of the distinct negative maxima at 278-279 nm and the shoulder at 289 nm (Fig. 13) due to the presence of tyrosines in a hydrophobic environment has been employed as a parameter for experimental evaluation of the kinetics[102]. This is also regarded as the most direct approach currently available.

It is evident from Fig. 13 that the CD spectrum of native ICSH is not equal to the algebraic sum of the spectra of isolated α- and β-subunits. Similar spectra of ovine ICSH treated under dissociating conditions, such as guanidine hydrochloride or acidic media, also give rise to a pattern which is equivalent to the algebraic sum of the CD spectra of the isolated subunits. These observations have led to the conclusion that definite structural changes occur upon dissociation of the native molecule, giving rise to alterations in the environment of the aromatic residues. It is also evident from Fig. 13 that all the CD changes occurring during dissociation are completely reversed upon reassociation.

These studies also permit one to follow the repair of mass by sedimentation velocity measurements and the repair of native conformation by means of CD spectra (Fig. 14). Dissociation in acid media is an extremely rapid phenomenon, the $S_{20,w}$ values dropping to a stable value of 1·54 from the original value of 2·54 within 2 hr. The dissociation kinetics, as indicated by CD spectrum changes, is essentially a first order reaction. During reassociation at *p*H 7·5, it is clear that the increase in mass due to the formation of the $\alpha+\beta$ complex occurs at a faster rate than the return of the native conformation. The repair of mass follows a second order reaction, while the repair of conformation is approximately of the first order. Therefore, the formation of the reassociated molecule can be visualized as a two-step reaction in which there is a rapid second order association of the two subunits to give a molecule of molecular weight ~30,000 which then undergoes a slow intramolecular rearrangement in the first order during which the aromatic amino acids get into a hydrophobic environment and become inaccessible.

The fiinal determination of the three-dimensional structure of the gonadotropins and TSH must await X-ray crystallographic studies. These would, of course, need methods for the development of suitable crystals. Although a few reports have claimed the successful crystallization of purified preparations of bovine TSH[103] and HCG[104], no confirmation is available yet.

X. Structure-Function Relationships

In the case of the glycoprotein hormones, the structure-function studies are meant to provide information on such aspects as the role of reactive side chain residues in subunit interactions and the ability

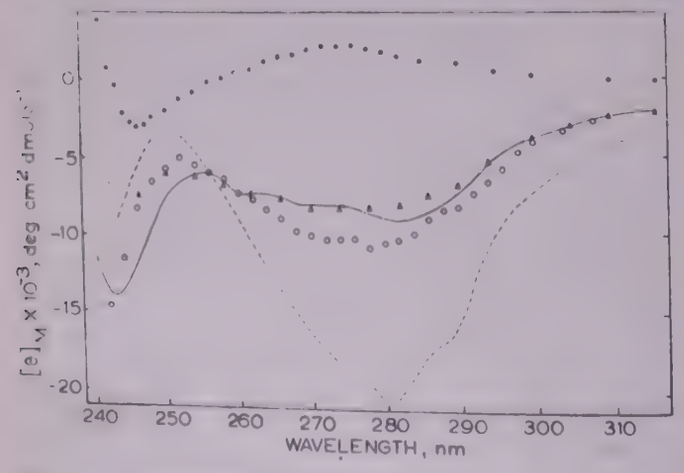

Fig. 13 — Circular dichroic spectra of ovine ICSH and subunits [– – – –, native ICSH; ○○○, β-subunit, ●●●, α-subunit,; ——— algebraic sum of α and β; ▲▲▲, native ICSH in 5*M* guanidine hydrochloride or *p*H 3·6. Taken from ref. 102]

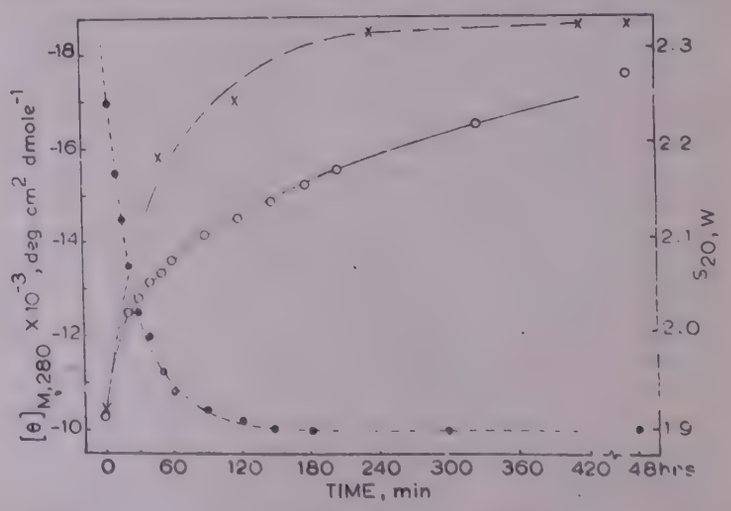

Fig. 14 — Kinetics of reassociation of ovine ICSH subunits [●-●-●, dissociation; ×-×-×, repair of *S* value (Mass); ○-○-○, repair of CD (conformation)[102]]

of suitably modified hybrids to interact with the receptor at the target level. Although a number of studies have been carried out in the past to evaluate the effect of chemical modifications on biological activity, many of these ought to be repeated in view of our current concepts of subunit structure. Thus, the availability of detailed information on the structure of the subunits of these hormones now permits a more meaningful interpretation of the effect of modification reactions. The results of some of the studies carried out recently are summarized in Table 10. Virtually all the studies have concentrated on the alteration of the polypeptide portions of the subunit. As can be seen, the majority of the investigations have been carried out with ICSH, a few on TSH and virtually none on FSH of any species. The most important point emerging from these limited studies is the crucial role of the α-subunit, a common subunit of all the glycoprotein hormones. Modification of the reactive residues in the α-subunit without affecting its ability to interact with its counterpart to form the dimer-reassociated molecule, however, results in more or less complete elimination of biological activity. The biological activity of the complex of native α+modified β is affected to varying degrees, depending on the modification introduced. The only modification reported to affect both recombination and activity is the removal of certain residues at the C-terminus of bovine TSH α by carboxypeptidase treatment[97]. In most cases, the immunological activity of the hormone or recombinants is either unaffected or marginally reduced.

The above studies demonstrate that while the requirements for the association of the subunits ($\alpha+\beta$-complex) are not so rigorous, the changes imposed on the α-subunit are important in influencing the generation of the correct conformation of the recombinant such that it can interact with the receptor at the target.

It became evident in the earlier discussion that the hormone specific β-subunit carries most, if not all, the features necessary for function. Though the isolated β-subunit might possess some binding ability to the receptor, viz. ICSH β (ref.53) and TSH β (ref. 60), its association with the α-subunit greatly enhances the binding of the complex and induces biological activity. The various structure-function studies indicate that the correct molecular conformation is exceedingly important for the generation of biological activity. The requirement of the correct molecular conformation in each hormone ($\alpha+\beta$ complex) must be quite stringent. Evidence from our biophysical studies[91] lends firm support to this. It was observed that the recombined molecule formed from the association of the subunits (prepared by the CCD method), though indistinguishable from the native hormone, had only 50% of the biological activity. Though our biophysical techniques could not distinguish the two molecules (native and reassociated), the biological assay system could discriminate the subtle differences in conformation.

XI. Concluding Comments

The discovery of the presence of quaternary structure in the glycoprotein hormones has added a new dimen-

TABLE 10 — STRUCTURE-FUNCTION RELATIONSHIPS OF ICSH, TSH AND HCG

Modification	Group affected	Hormone and remarks
Nitration	Tyrosine	Ovine ICSH[92], bovine ICSH[110], bovine TSH[110], HCG[111]. Alteration of activity by modification of the α-subunit is more severe than modification of β. Not all tyrosines in the native hormone are reactive.
Iodination	Tyrosine	Ovine ICSH[112], HCG[113]. In the native hormone the tyrosines of the α are exclusively affected.
Acylation	Amino group	Ovine ICSH[114–116]. Virtually eliminates activity of the native hormone. The +ve charge on the α-subunit, while not being important for binding with the β-subunit, seems to be essential for activity.
Cyclohexanedione	Arginine	Ovine ICSH[117]. Necessary for activity. Can be reversibly modified. May not be important for subunit interactions. Those in the α are relatively more important.
Carboxypeptidase	COOH-terminal	Bovine ICSH[97], bovine TSH[97]. Reduces activity. In TSH submits modification affects ability of both subunits to combine with native counterpart. Modified TSH α or ICSH α, however, can combine with native ICSH β, but no activity is generated.
Carboxamido derivative	—COOH groups	Bovine ICSH[118]. Dissociates the native hormone. —COOH groups in α are essential for combination with the β.

sion to the study of pituitary and placental hormones. The initial discoveries on the subunit structure of ovine ICSH and the subsequent demonstration of the interrelationship between TSH and ICSH have paved the way for rapid progress on other hormones in this class. Clearly, the most exciting aspect of the study of the glycoprotein hormones has been the elucidation of their complete amino acid sequences. Most of the data on the structure of glycoprotein hormones have appeared during the past five years and it is indeed remarkable to witness the tremendous impact it has made in clarifying the chemical, biological and immunological relationships within this group of hormones. Much of the information has come from studies on only a few species; despite this it is already apparent that similar results can be expected from studies on other species as well. However, there is clearly a need for more information, especially from non-mammalian species, to validate the evolutionary considerations.

It has been unequivocally demonstrated that all the well-characterized pituitary and placental glycoprotein hormones are composed of two chemically dissimilar subunits (α and β) which can be dissociated under a variety of conditions. The two subunits are not covalently linked. Both subunits contain carbohydrate. The isolated subunits have little activity that is typical of the hormones, in conventional assay systems. However, activity has been noted in some test systems. Initial amino acid composition studies and various biological hybridization experiments provided the first clue that one-half of the molecule (α-subunit) must be very nearly the same and has probably the same tertiary structure. Detailed amino acid sequence studies have confirmed this. Thus, for example, in the human, ICSH, FSH, TSH and HCG have an α-subunit whose amino acid sequence is virtually the same. In all the hormones, only one of the subunits, namely the β-subunit, has the structural characteristics that can give rise to a specific hormonal activity. Because of this property, it is usually referred to as the hormone specific sub-unit. Thus, the biological activity of a hybrid recombinant (α-subunit of one hormone + β-subunit of another) will be typical of the hormone from which the β-subunit was derived. This in no way rules out the existence of structural features in the α-subunit that would contribute to activity. As discussed in this article, the structural integrity of the α-subunit appears to be very important for the generation of a conformation that can induce biological activity. Thus, the α-subunit is acting more than as a simple inducer.

It has become clear now that ICSH, TSH, FSH and HCG are very closely related in structure. Although no definitive information is available yet on PMSG, it is interesting to predict that this hormone will fall into this pattern as well. It might well be possible that all these hormones have evolved from a common ancestral molecule. Whether this ancestral precursor happens to be a single polypeptide chain is not known. However, during the course of evolution, it is apparent that a combination of a single type of peptide chain with different but somewhat related chains has been utilized in the generation of different physiological functions.

The structural homology seen in ICSH β, TSH β, FSH β and HCG β, besides suggesting a common origin, also provides other important clues. The homologous areas undoubtedly must be connected with the binding of the α-subunit which is nearly the same for all these hormones. Therefore, the binding sites for the α-subunit must be identical in all the β-subunits On the other hand, parts of the sequence that are not common to one another must represent features involved in conferring hormonal specificity. Thus, it is reasonable to represent the glycoproteins as modelled in Fig. 1. The molecular topography necessary for interaction with the α-subunit is most probably the same in the three β-subunits. It is assumed that in this model, there is a subtle difference in the tertiary structure of the three hormone complexes to enable them to exert biological specificity. The combination of a β-subunit with the α-subunit results in the generation of a specific conformation that is typical of each hormone.

What is the physiological significance of the subunit structure in these hormones? This is the only class of hormones in which during the course of evolution, a true subunit structure has been organized to attain different biological functions. As is well-known from studies on other catalytically active proteins, it is only the oligomeric proteins which are subject to fine tuning by a mechanism that is usually characterized by the term "allosteric regulation". Whether any of the glycoprotein hormones is under such influences is presently unknown, but appears worth looking into.

Very little is known about the biosynthesis of gonadotropins and TSH. The presence of a subunit structure naturally raises a number of questions. How are these hormones biosynthesized? Is there a precursor like proinsulin or are the subunits themselves individually synthesized as precursors and then organized into a subunit structure during the process of secretion? We can expect answers to some of these questions in the years ahead. It is already becoming evident that administration of the releasing hormone, such as TRH (thyrotropin releasing hormone) or GnRH (gonadotropin releasing hormone), which are known to affect the tropic hormone synthesis and secretion in the pituitary, results in elevation of the circulating free α-subunit[105,106]. These have been detected by radioimmunoassays. In certain pathological instances, an abnormal secretion of a free β-subunit has been detected[107] and thus might serve as a diagnostic aid in the detection of certain neoplasms.

In most of the structural studies, it has been observed that heterogeneity in the polypeptide portion of the molecule is usually confined to the amino terminus of the α-subunit and COOH-terminal of the β-subunit. While other explanations are possible, one can also imagine that the two subunits were somehow connected together originally and during secretion an enzyme cleavage gave rise to the typical heterogeneity found. To account for the excess α-chain found in the pituitary and also liberated in certain treatments (cited above), it has been recently speculated that in the

pituitary, an α-subunit itself is the connecting piece between the two subunits[108]. Further experiments are necessary to substantiate these speculations.

Clearly much more work remains to be done on the structure of this interesting family of hormones. Determination of their tertiary structure by X-ray crystallographic methods would be very rewarding, but, in all probability, will not be realized for some time. The study of the nature of subunit interactions and interactions of hormones with the receptors in the thyroid gland and gonads is of fundamental physiological importance.

Finally, it may not be out of place to mention what may be a potential practical dividend of great consequence that has resulted from the various studies on the subunit structure of glycoprotein hormones. Because of the presence of an extra peptide fragment at the C-terminus of HCG β, which is absent in ICSH β (Fig. 8), it is conceivable that this portion of the molecule could be used as an antigen to possibly induce the formation of antibodies that might neutralize HCG in early pregnancy. Serious efforts in this direction are possibly underway in many laboratories. An alternative approach has utilized a so-called processed HCG-β subunit coupled to the tetanus toxoid to effect isoimmunization against HCG in humans[119]. It has been reported that antibodies formed in women were capable of neutralizing exogenous HCG without cross-reacting with the pituitary ICSH of the subject. Although the validity of inducing specificity for the antigenic sites of the HCG-β has been questioned[120], the approach, nevertheless, has practical implications. A careful substantiation of the claims of these provocative studies[119] will undoubtedly provide an additional approach in controlling human fertility.

The discovery of the quaternary structure of the glycoprotein hormones and the establishment of their inter-relationships will undoubtedly provide a strong impetus to a long series of studies on their biochemistry and physiology.

Summary

The well-known glycoprotein hormones of the pituitary and placenta greatly resemble one another in molecular architecture. All are oligomeric proteins consisting of two non-covalently linked dissimilar subunits. One of the subunits, designated as the α-subunit appears to be nearly identical in all the three hormones, lutropin, follitropin and thyrotropin. The other subunit, designated as the β-subunit, is referred to as the hormone specific one and is different in each hormone. Both subunits contain carbohydrate. Dissociation of the hormone results in a conformational change which is accompanied by virtually complete elimination of the biological activity. The activity can be restored upon suitable recombination of the protomers. Interspecies as well as inter-hormone hybrids can be made. In each case, the biological activity generated depends upon the choice of the β-subunit. The complex will have the activity of the hormone from which the β-subunit was derived. The β-subunit has the basic requirements to interact with the receptors at the target site, but combination with the α-subunit, possibly, enhances binding and allows full expression of activity. The amino acid sequences of the two subunits of the hormones from different species have been determined. In the human, the sequence of amino acids in lutropin α, thyrotropin α, follitropin α and chorionic gonadotropin α, is virtually identical. Homologies can also be seen in the hormone specific β-subnit. All the hormones in this class could possibly have evolved from a singe precursor.

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REVIEWS

RUDOLF PEIERLS AND THEORETICAL PHYSICS : PROGRESS IN NUCLEAR PHYSICS, Vol. 13, edited by I.J.R. Aitchison & J.E. Paton (Pergamon Press Ltd, Oxford), 1977. Pp. vii+119. Price £5·00; $10·00

Prof. Sir Rudolf Ernst Peierls is one of a small group of theoretical physicists doubly blessed in that they were outstandingly gifted and they began their research careers just after the advent of quantum mechanics. Some others that come to mind are Landau, Bethe and Oppenheimer. Quantum mechanics had brought about a great unification in physics and a vast variety of problems became amenable to solution or were seen in a completely new light. As a result, each of the doctoral theses of these physicists essentially inaugurated a new fertile field of investigation.

Peierls' contributions to physics are remarkable both because of their range and because of the deep insight into phenomena that they show. He is responsible for basic advances in solid state physics, nuclear physics, phase transitions, field theory and during World War II in problems of nuclear energy. The book under review gives us an account of all these achievements, but even more, the picture of a warm and fine person able to communicate his enthusiasm and ideas to others and work with them comes across very clearly. Out of eight talks delivered at a symposium in Oxford on the occasion of his retirement in 1974, and presented in this book, no less than five are accounts of areas and problems where Peierls himself made critical contributions. The piece by O.R. Frisch on the early stages of the nuclear chain reaction is largely non-technical and on the personal level, but it makes clear the magnitude of Peierls' contribution in this field. R. Berman gives a nice exposition of Peierls' famous invention — the Umklapp processes. G.E. Brown's description of the Kapur - Peierls resonance theory of 1938 shows the relevance of those ideas in tackling the currently interesting problem of isospin analog states in nuclear physics. The talks by S.F. Edwards and D.J. Thouless are on the somewhat related topics of 'Disordered systems' and 'Phase transitions', again areas in which Peierls made important contributions very early.

This is a nice book well worth possessing, not necessarily because one might learn a great deal of physics from it, but rather because of the portrait of Peierls that it presents.

N. MUKUNDA

THE UNIVERSE : GEOPHYSICS AND ASTROPHYSTICS MONOGRAPHS, Vol. 11 by Josip Kleczek (D. Reidel Publishing Co., Dordrecht, Holland), 1976. Pp. viii + 259

This is an ambitious book, "an attempt to interpret the structure and evolution of the universe in terms of elementary particles and their interactions." It is aimed at students and teachers of astronomy with the hope that it might interest a wider audience. The first three chapters are devoted to elementary particles, the forces between them and the states of matter arising therefrom. The remaining half of the book consists of two chapters entitled "Structures" and "Evolution" which cut across the conventional divisions, dealing with the entire range from hadrons to galaxy clusters and the universe.

The entire book is densely packed with information, much of it derived from very recent work. It is unlikely that a student could digest all this without a good deal of comment and motivation which a teacher using the book for a course would have to supply. The absence of references, even to reviews, is a serious drawback. No book with this scope could hope to give a self-contained account which would satisfy the majority of readers.

The emphasis on tracing phenomena back to the four fundamental interactions has resulted in a good deal of superficiality. Surely it is not very helpful to say that the human body is built up of "10^{28} to 10^{29} elementary particles interacting strongly in atomic nuclei and electromagnetically in atoms, molecules, and tissues". Intermediate levels of description like hydrodynamics, thermodynamics, and chemical affinities afford more insight into complex systems but do not find a place in the philosophical perspective of this book.

In general, the book is at its weakest when giving explanations and tracing interrelationships. Quite often, one finds words like 'sub Alfvenic' and 'shock front' cropping up in place of a physical picture. It is quite clear that the book has not been written having a reader in mind with a specific background and specific needs. The reader who can discern the essence of electromagnetism from seeing Maxwell's equations in parentheses on page 61 surely does not need to be told on page 81 that he would fly off the earth but for gravity.

Any book with this theme runs the risk of being compared with Gamow's 'One Two Three Infinity' and 'Creation of the Universe' — out of date as they are. The force, style and insight shining through these books make them unsurpassed as an inspiring introduction to the scientist's view of the Universe. The book under review is at its best a collection of uptodate facts and the results of recent theories. A worthy successor to Gamow is still awaited.

RAJARAM NITYANANDA

PRACTICAL TECHNIQUES FOR SAVING ENERGY IN THE CHEMICAL, PETROLEUM AND METALS INDUSTRIES by Marshall Sittig (Noyes Data Corporation, Park Ridge), 1977. Pp. xiii + 525. Price $ 48.00

The book is very timely, specially in these days of energy crisis, and energy saving consciousness. It is divided into a number of chapters dealing with brief descriptions of the process technologies involved in a number of industries, and the recommendations regarding energy saving or conservation in these. Some of the industries are metals, steel, aluminium, foundry, ferro alloy, zinc, lead, alkalies, industrial gases, inorganic chemicals, plastics, synthetic rubber,

fibres, soap and detergents, paint, coaltar chemicals, fertilizers, agricultural chemicals, carbon black and petroleum as well as coal products. A few of the energy conservation measures include design, process and operation modifications, improvements in maintenance and insulation as well as good housekeeping, waste utilization, computer control and so on.

It is difficult to do justice to the author in a short review by citing recommendations with regard to all industries, and the reviewer, perforce, has to be selective. In the steel industry, some of the energy saving measures recommended are dry quenching of coke, preheating of coal prior to charging in the coke oven, increased blast furnace gas recovery, injection of coal into blast furnaces, installation of basic-oxygen steel making furnace in place of the older open hearth, increased use of pellets, greater attention to ash, sulphur content of coke, and so on.

In the industrial gases industry, the energy conservation measures include the use of more efficient compressors, heat exchangers, and distillation columns with less pressure drops, reducing product purity to no more than contract level, and so on.

In the nitrogen fertilizer industry, some of the measures advocated are removal of CO by methanation using Ni catalyst, instead of copper-liquor scrubbing, and use of chemical or physical adsorbents, such as Alakazid or Rectisol, for the removal of sulphur compounds while using oil feedstocks, active programme in housekeeping, maintenance, process control, energy balancing, etc.

In the soap and detergent industry, energy saving measures advocated are in unit operations and in spray-drying to produce synthetic detergents. Improved formulations tend to be more energy intensive.

In the carbon black industry, the author quotes Battelle estimate of about 40% reduction in specific energy consumption by measures such as use of reactor gas for drying, generating steam, and energy improvements with respect to the common practice of water-quenching in furnace black production.

As regards petroleum and coal products industry, some of the approaches suggested are generation of high pressure steam in the refinery boiler, and making the excess steam available for external consumers, generation of steam at high pressures being more economical than generation at low pressures. More efficient combustion control is effected by control of excess air through good instrumentation. Improved boiler efficiency is effected by replacement of old boilers with new, installation of modified blowdowns that control the concentration of solids in boiler water systems, preheating boiler feed water, and so on. The use of antifoulants to prevent attachment of deposits inside water coolers in exchangers improves heat transfer. Attractive economic benefits result from closed loop computer control of complex units, such as fluid catalytic crackers and reformers.

Notable among the general measures advocated is recycling. A factor that mitigates against energy saving is the unavoidable necessity of meeting the environmental regulations, e.g. the desirability of producing biodegradable detergents.

The material for the book has been collected from very recent publications (1974-1976), and this makes the book very valuable. The get-up of the book is excellent. The reviewer recommends the book strongly not only to industries which are interested in energy saving, but also to researchers in the most discussed field of energy.

K.A. KINI

PARTICLE BOARD MANUFACTURE : Chemical Technology Review No. 84 by Howard A. Miller (Noyes Data Corporation, Park Ridge, USA), 1977. Pp. x + 315. Price $39·00

Ever since technologists learnt to utilize polymeric materials (initially natural rubber), there was a concerted effort to bring down the price of the finished product by adding cheaper ingredients known as fillers. However, more systematic investigation revealed that the fillers sometimes enhanced the useful properties of the final product, and thus extend the range of its application. In the present volume, the author has selected and systematically arranged the US patents pertaining to the application of chips, ribbons, shavings and splinters of wood of various types in the manufacture of board; resins of various types have been used as the binding medium. The subject matter has been classified under the following six heads: (1) Phenol-formaldehyde and urea-formaldehyde binders, (2) Polyurethane, ammonia and other binding processes, (3) General processing and manufacturing techniques, (4) Laminations and decorative overlays, (5) Speciality molded products and other processes, and (6) Other fillers and components for board manufacture. The last one includes application of bagasse, rice hulls, vermiculite, plant fiber residues, etc. Application of these materials is of particular interest to India where bagasse is available as a waste material of the sugar industry and mica waste from the mica mining operations. It is interesting to record that during the Second World War, when there was an emphasis on conserving metal, very large number of processes were developed utilizing a variety of agricultural wastes, e.g. bagasse, soft woods of various types, jute waste, mica, etc. [*Patented inventions of CSIR* (Council of Scientific and Industrial Research, New Delhi), 1951] (*Indian Patents No.* 27714, 28277, 28281, 28306, 28428, 29966, 33786, 41878, 33077, etc.). These inventions not only helped to tide over the difficult war-time shortages, but also led to further developments and establishment of new industries.

The author notes that patents provide an excellent starting point for the next investigator, for it is a creative source of ideas for those with imagination. The present volume is a kind of annotated bibliography of the subjects under discussion. The subject matter is arranged systematically. It is a valuable digest of the technical patented literature and is certainly a welcome and timely publication. The volume is also attractively printed, bound and indexed.

M.R. VERMA

Notes & News

Holographic fringe stabilization

A basic difficulty in many holographic recording systems for use in vibration analysis and interferometric testing is the lack of fringe stability in the hologram recording plane. This instability may be due to atmospheric disturbances like thermal drifts, vibration of components, swifts in frequency of laser used, etc. The instability may result in diminution of fringe contrast and diffraction efficiency of the hologram recorded. *Posteriori* image correction of the hologram by use of holographic filters [Stroke, G.W., *Introduction to Coherent Optics & Holography* (Academic Press Inc., New York), 1969] is not universal and reliable in application. David R. Mac Quiggo of Lawrence Livermore Laboratory, California (USA) has now devised a phase shifter network actuated by a feed-back amplifier for *in situ* correcting of the phase anomalies (due to instabilities cited above) of the hologram.

The technique uses a phase shifter network interposed in the source beam (S) between the object and hologram in a conventional recording set-up using a coherent reference beam (R). The phase shifter is made up of a 12·7 mm glass plate rotated by an electromagnet. A control grating beyond the hologram mixes the signals R and S (forming high contrast fringes) and feeds to a photodiode coupled to a lock-in-amplifier which electronically detects the phase of the fringes formed in the hologram plane. The control grating also enables introduction of known shifts in the phase of fringes in hologram (The use of a grating in place of optical focussing devices enables better light gathering from the hologram output, i.e., for instance, with a fringe spacing of 3 μm, a 10 mm grating gives a light magnification as high as 7). A high frequency oscillator (lock-in-amplifier) coupled to the phase shifter generates a high frequency oscillation for varying the phase of the fringes in the hologram plane. The resulting phase change is detected by the photodiode coupled to the lock-in-amplifier. In the absence of phase changes introduced by the shifter, the photodiode is locked on to the theoretical minimum of fringe intensity (Advantage of using this set-up for minimum is that the phase setting is unaffected by laser intensity fluctuations, etc.).

In operation, the system instabilities, cited above, introduce arbitrary phase changes into the beams R and S, as a result of which the photodiode detects the phase anomaly and the lock-in-amplifier generates a corresponding error-signal which then actuates the phase shifter. The phase shifter introduces a compensating phase change into the beam S, nullifying the phase anomaly. In a typical set-up, phase settability and readjustability were found to be within 5° for a dichromate-coated gelatin hologram using a control grating (rotated by a differential micrometer) of 3 μm period [*Appl. Opt.*, **16** (1977), 291].

Heavy ion transfer reactions

In the reactions between heavy ions it is usually found that the cross-sections are more sensitive to particular aspects of nuclear structure than the corresponding reactions with light projectiles; this makes them useful tools in nuclear spectroscopy.

An example of this is the spin-dependent effects in some transfer reactions. If a particle is transferred from a (l_2, j_2) state in the projectile to a (l_1, j_1) state in the residual nucleus the angular momentum selection rules allow several values of the transferred angular momentum (L), and these depend on whether the angular momentum given to the residual nucleus is $j_1 = l_1 + \frac{1}{2}$ or $j_1 = l_1 - \frac{1}{2}$. In the particular case when $l_1 = 0$, $L = l$ and it is possible to study the dependence of the cross-section on j_1 for given value of L.

Such a study has been reported by a group at the University of Minnesota for the ^{28}Si (^{19}F, ^{16}O) ^{31}P reaction at 60 MeV. In this reaction three nucleons are transferred, but it is a good approximation to consider these as a triton-like cluster and thus retain the simplicity of a one-nucleon transfer reaction. The experimental cross-sections for the $L=2$ transfers to the lowest $(3/2)^+$ and $(5/2)^+$ states in ^{31}P were found to be markedly different, showing how the reaction can depend on j as well as L.

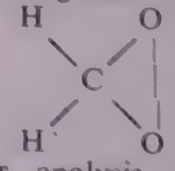
The first distorted wave calculations, made with a finite range interaction and taking recoil into account, did not give a satisfactory fit to the data. Also there was no improvement when inelastic excitation of the projectile was included by making a full coupled channels calculation. A satisfactory fit was obtained when spin orbit potentials were included in the distorting potentials in the incident and exit channels. The fit was very little affected by the inclusion of inelastic excitations.

Further studies of similar reactions will be needed to confirm that the essential physics of the reaction has indeed been well understood and if this is the case, such reactions may prove to be a powerful spectroscopic tools for determining the spins of the final states in the residual nuclei [*Nature, Lond.*, **268**(1977), 18].

New chemical detected in smog formation

The first example of a new class of small-ring compounds has been dected as a short-lived intermediate in photochemical smog reactions. The compound, dioxirane, was found while studying the reaction of O_3 with ethylene, an important reaction in smog formation.

The dioxirane molecule is very simple looking and is as follows:



Computer analysis of reaction rates and product concentrations for the ozone-ethylene reaction revealed that 90% of the reaction products were molecular fragments rather than free radicals. This finding contradicts most current reaction mechanisms, which call for the formation of large numbers of free radicals, but it supports a mechanism proposed

earlier, in which case dioxirane is an intermediate.

Ozone-ethylene reaction was performed in a specially constructed microwave absorption cell cooled to −196°C. Under these conditions, the dioxirane molecule is stable enough to be detected by microwave spectroscopy. Experiments were then repeated at low temperature and by mass spectroscopy analysis an intermediate was detected, the charge-to-mass ratio for which is consistent with dioxirane [*Chem. Engng News*, **55** (46) (1977), 5].

Atmospheric ozone monitoring

Measurement of total ozone (O_3) content and mapping of concentration versus altitude profile in the upper atmosphere is of considerable importance in view of gaseous pollution tending to deplete ozone layer. The measurement is based on IR absorption of solar radiation by the atmosphere, especially at the wavelength region 9·5 μm where the ozone has strong absorption (ν_3) bands. The conventional Dobson IR-radiometer is not quite suitable for ozone monitoring owing to low accuracy and doubtful performance when afflicted with atmospheric disturbances, aerosols, etc. However, two physicists of the National Aeronautics and Space Administration, Washington DC have avoided these limitations through an improved measuring technique (with high signal-to-noise ratio) based on solar heterodyne IR-radiometer [Payton, B.J., *IEEE J. Quant. Electron., QE*-11 (1975), 569]. The heterodyning of the IR absorption spectrum is achieved by mixing the output from a tunable infrared CO_2-laser (local oscillator) coupled to a photomixer and IF-electronics. The radiometer enables measurement of solar absorption at selected wavelengths with a spectral resolution of 0·001 cm^{-1} (equivalent to half-width of O_3 at 10 mbar altitude level). Heterodyning of the radiometer detector output with the tuned CO_2-laser emission set at IR-wavelengths (P_{18}-P_{24} lines) ranging 9·4-10·5 μm with corresponding absorption lines of O_3 in this range, enables higher sensitivity of monitoring. The sensitivity of the device is found to be in terms of ozone cumulative abundance as small as 10 parts per billion km. The heterodyne O_3 detection technique was found to be reliable at low altitudes as well as at the stratosphere up to 35 km. The device has a high spectral resolution with a precision up to 0·006 cm^{-1} in the determination of IR absorption frequencies. [*Science*, **197** (1977), 1275].

Chinese Astronomy

This is the first issue of a bi-annual cover-to-cover translation of *Acta Astronomica Sinica* (in Chinese) starting from June 1977 from the Pergamon Press, Oxford (England). Though it is widely known that the *Acta* journal publishes advanced research papers in the field of astronomy carried out in China, it was rarely consulted because of the language barrier. Prof. T. Kiang, Dunsink Observatory, Dublin (Ireland) is the translator from Chinese and the English text of *Chinese Astronomy* is edited by Dr G. St. Mark also from Dublin.

The inaugural issue of *Chinese Astronomy* commences with the translation of papers (inclusive of research notes, review articles, etc.) in the *Acta* of 1976 (Vol. 17, No. 1); besides, the issue includes a certain outstanding papers from back volumes.

The papers in this issue cover a wide variety of subjects, such as planetary motion, dynamics of artificial satellites, comets, meteorites and galactic wings, galactic cosmic ray bursts and pair-production in superdense stellar objects, cosmological models and evolution of galaxies.

The annual subscription of the journal is US $ 105. Further details can be obtained from Pergamon Press Ltd, Headington Hill, Oxford OX3 OBW (England).

National Institute of Oceanography (NIO), Goa

The annual report of the institute for 1975 reveals that the institute investigated 18 projects with emphasis on coastal zone management, physical processes, air-sea interaction, extraction of active compounds from seaweeds, exploration of mineral resources, aquaculture, oceanographic instrumentation, and data processing.

The first phase of the United Nations Environment Programme on marine pollution monitoring and marine living resources assessment for the Indian Ocean region was initiated. Ten sampling stations were established along the west coast of India for observations on the pilot project on monitoring of oil pollution under the framework of the Integrated Global Ocean Station System. Regular sampling and monitoring of tar ball deposits along the west coast were continuing. Observations on oil spills in the open sea are being carried out by the Shipping Corporation of India and Scindia Steam Navigation Co. Ltd.

Sponsored projects undertaken by NIO include: Surveys for Zuari Agro-Chemicals proposed effluent pipeline route in the Cola Bay, Goa; Model studies of Mandovi Zuari estuaries and Cumbarjua Canal; Hydrographic studies in the inner harbour of Cochin Port; Determination of suitable points in the sea off Mangalore for the discharge of treated waste material for pollution control off Karwar; Oceanographic survey of Narara Bet in the Gulf of Kutch; and Contract sorting of zooplankton.

Under a project on physical processes ocurring in the seas around India, data collected during Indo-Soviet Monsoon Experiment (1973) and *Darshak* Oceanographic Expedition (1973-74) were analyzed. Studies on the light penetration in the coastal waters and littoral drift and nearshore circulation along Goa coast were also carried out.

The investigations relating to chemical oceanography were carried out on: (i) inter-relationships of organic and inorganic constituents of estuarine and inshore waters around Goa and the coastal offshore and deep sea regions of the northern Arabian Sea; (ii) chemistry of pharmacologically-active components of marine plants and animals; (iii) pollution problems; and (iv) improvement of efficiency of solar desalination stills.

Geological and geophysical surveys were carried out to assess the

petroleum and mineral prospects of the western continental margin of India. The sedimentological and palaeontological studies on the seas around India were also carried out. Seventy sediment samples were analyzed for organic matter and foraminiferal diversity. It was found that rotalid and miliolid foraminifera dominated in the beach and water-tidal zone, whereas in the polluted region, rotalids decreased with the increase in miliolids and species like *Trochamina, Nonionella* and *Bucella*. Because of altered environmental conditions, rotalids and miliolids showed vesicles in their chambers, discolouration due to fillings and decalcification of their ornamentation.

Studies were carried out on the aquaculture in the waters of Goa and Cochin. Laboratory and field studies were carried out on the bioenergetics of some marine and estuarine forms. Biogeography of the zooplankton in the Indian Ocean was studied with regard to the systematics and zoogeography and ecology of zooplankton, and environmental preference, species association, abundance and diversity.

The new instruments developed at NIO are: tide and wave recorder and counter, operational depth meter, and a conductivity-type salinometer. The salinometer can read salinity directly, has a range of 0-38‰, and a sensitivity of ±0·05‰.

Eighty-one research papers were published during the year.

Announcements

● *The Tenth Indian Rubber Conference* organized by the Indian Rubber Manufacturers' Association will be held at Baroda during November 1978. Various aspects of chemistry, technology, engineering of rubbers, compounding ingredients machinery and testing equipment, etc. applicable to rubber industry will be the major areas of discussion during the conference. Further information regarding the conference can be had from Dr W. Millns, Director, Indian Rubber Manufacturers' Research Association, Plot No. B-88, Road No. 'U', Wagle Industrial Estate, Thana (Maharashtra).

● *The Second International Colloquium on Electron Beam Welding and Melting* organized by the Commissariat á l'Energie Atomique and the Institut de Soudure will be held in Avignon during 5-8 September 1978. Problems connected with electron beam welding and melting will be discussed during the colloquium. Further information regarding the colloquium can be obtained from Dr M. Buffereau, Secrétariat Général du 2 émé CISFFE, Commissariat á l'Energie Atomique, DMECN, BP 2-91190 Gif-Sur-Yvette (France).

● *The Third International Congress on the History of Oceanography* will be held in Woods Hole Massachusetts, USA, during 22-26 September 1980. The congress is a part of the 50th anniversary celebrations of the Woods Hole Oceanographic Institution, Massachusetts and will be followed (25 Sept. – 4 Oct.) by an assembly on current and future oceanography.

Further information regarding the congress can be had from Dr Danial Marriman, Chairman Organizing Committee, The Third Internatonal Congress on the History of Oceanography, 298 Sperry Road, Bethany, CT. 06525.

● *A Seminar on the Role of Chemical Engineers in Rural Development* organized by the Coimbatore Regional Research Centre of the Indian Institute of Chemical Engineers will be held at Coimbatore during 4 and 5 August 1978. The topics of discussion at the seminar will be: (i) Utilization of agricultural products (including agricultural wastes); (ii) Rural industrialization and environmental pollution; and (iii) Industrial engineering applied to small scale industries. Further information regarding the seminar can be had from Dr V. Subramaniyan, Honorary Secretary, I.I.Ch.E., Coimbatore Regional Centre, Department of Chemical Engineering, Coimbatore Institute of Technology, Coimbatore 641 014.

● *A National Solar Energy Convention* of the Solar Energy Society of India, organized by the Central Salt & Marine Chemicals Research Institute, Bhavnagar, Bharat Heavy Electricals Ltd, Central Electronics Ltd, Dept. of Science and Technology, Jyoti Ltd, and Tata Energy Research Institute, will be held at Bhavnagar during 20-22 December 1978. Discussions during the convention will be in the following major areas: (i) Photovoltaics, photochemistry, photobiology and radiation; (ii) Solar flat plate collectors; (iii) Solar concentrators; (iv) Solar thermal power systems; (v) Space heating and cooling; (vi) Energy storage; (vii) Selective coatings; (viii) Rural applications; and (ix) Industrial applications.

The last date for submission of papers for the convention is 30 July 1978. Further information can be had from Prof. K.S. Rao, Secretary, National Solar Energy Convention, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002.

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